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# Selected Translations of the Russian Literature on the Electrogeochemical Sampling Technique called CHIM (Chastichnoe Izvlechennye Metallov)

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# Introduction

by

D.B. Hoover and D.B. Smith

As part of our research into new methods for the assessment of mineral deposits, the U.S. Geological Survey has recently begun investigation of the CHIM method. As part of our studies, translation of a Russian manual on the CHIM methodology and eight articles from the Russian literature were translated to provide background for our own research. The translations were done by Earth Science Translation Services of Albuquerque, New Mexico, and are presented as received, without editing on our part. Below is a bibliography of the translated articles.

For approximately the past 20 years Russian geoscientists have been applying an electrogeochemical sampling technique given the Russian acronym CHIM, derived from Chastichnoe Izvlechennye Metallov which translates as "partial extraction of metals". In this technique a direct current is introduced into the earth through collector electrodes similar to "porous pots" used in electrical geophysical applications. The solution in the cathode is dilute nitric acid, and current is passed through the cathode for times ranging from 6 hours to 48 hours or more. Electrical connections to the nitric acid are made through an inner conductor that is typically spectroscopically pure graphite. At the cathode, mobile cations collect on the graphite or in the nitric acid solution, both of which serve as the geochemical sampling media. These media are then analyzed by appropriate methods for the ions of interest. In most applications of the CHIM method only mobile cations are sampled, although Russian literature does refer to collection of anions as well. More recently the CHIM method has been applied by the Peoples Republic of China and the Indian Geological Survey.

The literature indicates that the method has advantages over other geochemical sampling techniques by providing increased sensitivity to the metals being searched for, especially where deposits are covered by substantial overburden. In some cases success has been claimed with overburden in excess of 500 meters. The technique appears to have been applied principally to exploration for base- and precious-metal deposits, but does not appear to be limited to these. References are made in the literature to its application in the search for nickel, cobalt, molybdenum, uranium, tin, REE, tungsten, berylium, and oil and gas.

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USSR MINISTRY OF GEOLOGY

Research and Development Organization "Geotekhnika"

ALL-UNION RESEARCH INSTITUTE OF
EXPLORATION TECHNOLOGY (VITR)

# THE EXPLORATION OF ORE DEPOSITS BY THE CHIM METHOD

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The present manual describes the methodology of field observations using the method of partial extraction of metals (CHIM). In the report, we briefly cover the physico-chemical basis for the new method, and the principles involved in field operations, the equipment used, and the techniques associated with the analysis of the extracted mass of metals. Special attention is given to the safety of operations and to the design, documentation, and reporting associated with investigations performed.

The method is feasible for explorations of deep-seated polymetallic, copper, nickel, gold, and other deposits covered by sediments 100 m thick or more (the aureole method), and for exploration of deposits in order to identify ore intervals in boreholes either drilled without core sampling or with low core recovery (logging method).

18 Figures, 2 Tables.

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LITERATURE ON THE CHIM METHOD

## INTRODUCTION

In contemporary environment, covered deep-seated ore deposits have become the primary source of reserve growth in the supply of natural resources. The complexity of the problems associated with deep exploration has increased over time. Expenditures of time and money in the discovery and development of each new target have also increased. This necessitated the development of methods capable of detecting ore deposits at appreciable depths under thick Mesozoic-Cenozoic deposits cover. The geoelectrochemical method of partial extraction of metals, CHIM, is one of a number of such methods which have been proposed in recent years. This method allows the detection of ore targets under 100 m or more of unconsolidated overburden and simultaneously permits the evaluation of the ore grade and of the extent of the ore zones. The CHIM method can also be used to determine the nature of geophysical anomalies or, as is often said, to "sort them into ore- and non-ore-related anomalies."

The CHIM method proved useful for logging the walls of drillholes in order to identify ore intervals when the yield of core was low or when no core was available from the drilling. In contrast to many logging methods, the logging version of CHIM allows one to directly record higher grades of lead, copper, nickel, and other ore elements downhole. The method also works well under the following conditions: 1) under various cavernous conditions with respect to borehole wall; 2) when various anti-vibrational lubricants are used; 3) where the ore is hosted by graphitized and pyritized (pyrrhonitized) rocks; and 4) where ores of different compositions and textures are represented by both electroconductive and non-electroconductive minerals.

The CHIM-10 station was designed for applications of the CHIM method in the field. This station is serially produced by the Tuimaza Factory for Manufacture of Geophysical Instrumentation and Equipment. For rapid analysis of the extracted elements, the field polarograph FPL-I was designed. The polarograph is manufactured by the Experimental facility at VITR and can be set up as a part of a CHIM-10 station. Implementation of the method and of the CHIM station is underway in several regions of our country.

In this manual, we have for the first time systematized the information concerning the methodology of the field operations, the equipment, the planning and organization of the exploration survey using the new CHIM method, and the documentation and reporting associated with the operations.

## I. PHYSICO-CHEMICAL BASIS; PURPOSE AND AREAS OF APPLICATION

I. I. The method of partial extraction of metals is based on the dissolution of minerals under the influence of an electrical current, subsequent transport (migration) of dissolved, charged components in the field of the current, and the accumulation of extracted elements at the points where the external power sources connect to the rocks, and also in certain other areas of the hosting environment.

The electrochemical solution of minerals with metallic atomic linkage occurs as a result of the electrode reactions which take place at the boundary between the solid and liquid phases when a current is passed through the minerals. A typical reaction of an anodic solution of sulfides (MeS) is the process:

$$MeS \rightarrow Me^{2+} + S^{0} + 2e \qquad (a)$$

The created metallic ions and also the sulfur in the reaction zone can be oxidized to still higher valences, forming $Me^{3+}$ ions, polythionates, and sulfate ions. The combined anode reactions can be described by the equation:

$$MeS + 4H_2O \rightarrow Me^{3+} + SO^{2-}_4 + 8H^+ + 9e \qquad (b)$$

In the cathode process, metals are reduced to the elementary state, while sulfur goes into solution in the form of the sulfide ion

$$MeS + 2e \rightarrow Me^{0} + S^{2-}. \qquad (c)$$

When the electric current ceases, the metals are converted in the presence of oxygen to oxides and hydroxides and the sulfur is converted to polythionate and $SO_4^{2-}$.

Dissolution of minerals with covalent and ionic atomic bonding is still poorly understood. One of the dissolution mechanisms is a shift in equilibrium between the solid and liquid phases which occur when ions forming easily dissolved compounds with components of the solid phase, are introduced into the pore space by the electric current. Ions of sodium, chlorine, and several other elements usually facilitate the dissolution of carbonates and silicates. Quite the contrary, the introduction of iron ions and $CO_3^{2-}$ often results in the formation of new solid compounds which fill the porous space and lead to shrinking and closing of the pores.

The ions and colloids created as a result of the electrochemical solution of the minerals move in the field of the electrical current in the direction of the current or against it, according to their charge: positively charged components move toward the negative terminal of the external current source, while negatively charged components move toward the positive terminal. The speed of movement of the charged particles is proportional to their mobilities and the field potential. The speed also depends upon the properties of the medium: porosity, moisture, the structure of the porous space, etc.

Additional phenomena arise in porous rocks as a result of electrokinetic, thermal, and other processes associated with the passage of current. In certain situations, these phenomena cause a slow-down of the movement of ions, while in other situations they cause an acceleration of such movement. As a result of the influences of all of the factors mentioned, the total mobility of the ions in rocks can vary over a wide range (from parts of $cm^2$ per hour to tens of $cm^2$ per hour).

As a consequence of the interaction of components migrating into the field of current with the solid phase, and as a c onsequenceof the interaction of one component with another and also because of the effects of electrokinetic and other factors, the transport of components within the overall flow takes place at distinct rates which vary over time, which vary along the section of the flow, and which vary with respect to the direction of movement. A change in the mobility rate of an individual component will be accompanied by corresponding changes in the movements of other components. The differential mobility of each type of ion at different times and at different locations within the space varies over a wider range than does the total mobility associated with the ions. The possibility of selectively influencing (controlling) ion movements in large rock masses has been inadequately studied thus far.

Accumulation of the emerging components takes place at sites of active interaction of mobile ions with the surrounding medium, and also in areas of decreased electric-field potential. They accumulate most intensively at points of contact between the the external electric source and the rocks. Electrode reactions proceed on surfaces of the metal electrodes through which the current was introduced into the ground. The electrode reactions can differ depending upon the composition of the electrode, the surrounding medium, and the incoming components. The arriving components participate in reactions and accumulate in the form of reaction products. If arriving ions do not participate in the electrode process, then the substances initially accumulate in the same form in which they arrived. Then, as their concentrations increase, they can begin to interact with other products of the electrode reactions and also with the surrounding environment, themselves transforming in the process into new compounds. The substances formed in the electrode zone can vary. A portion of them play a part in subsequent enrichment with arriving components. The enrichment is keeping with the electrode process and with the reactions involved in the interaction of the arriving substances and those being again transformed. However, cases are possible where the products of the electrode reactions are ions transported in the field of the current toward the arriving substances. If the ions mentioned form poorly soluble compounds with the components being introduced, the latter accumulate at various distances from the electrode. The further away the accumulations are from the electrode, the greater the distance the ions, created during the electrode process, have been transported. Among the ions mentioned, the hydroxyl ions formed as a result of the cathode reaction splitting the water molecule is of special significance:

$$2H_2O + 2e \rightarrow H_2 + 2OH^-$$

The hydroxyl ions block the arrival of positive metallic ions, which then accumulate some distance from the electrode. Special reactions could eliminate the emerging $OH^·$ and thus facilitate the accumulation of metals right beside the electrode. The electrode should be appropriately equipped to ensure regulation of the elements associated with accumulation processes near the electrode. Such operationally equipped electrodes are designed for the CHIM method and referred to as element-receivers (ERs).

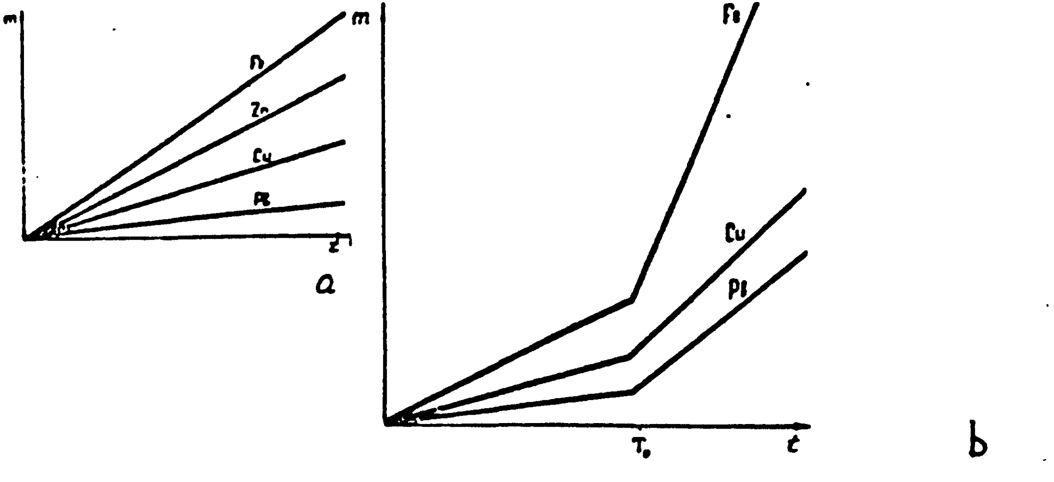

Fig. 1. Schematic geoelectrochemical hodographs for homogeneous barren rocks (a) and rocks with mineralization (b).

Inferences can be made concerning the process of element accumulation on the basis of a geoelectrochemical hodograph (Fig. 1) characterizing the dependence of the mass (m ) of the accumulating element upon time (t ). For homogeneous environments and electrical fields of differing structure, the hodograph for each component takes the form of a straight line. When conditions involving depletion of that component are approached in the treated volume of rock, the arrival of ions to the zone of accumulation ceases. At this point in time, the hodograph flattens out and changes to a straight line parallel to the time axis (the abscissa). The increase in mass per unit time dm/dt reflects the rate of accumulation of the corresponding element. The higher the rate of this accumulation, the higher the concentration (C) of this element in the volume being treated:

$$dm/dt = pC \ (I) \quad \text{or} \quad C = P \ \ dm/\ dt \ \ (2), \ \text{where} \ P = \frac{I}{p}$$

The functions P and p depend upon many factors: the forms of occurrence of the elements in the volume being studied, their quantitative ratios with respect to one another, conditions of electrochemical dissolution, the character of the ions movement in the field of electrical current, the specific features of the reactions at the sites of accumulation, etc. Nevertheless, the values of P and p remain constant over a fairly wide range of conditions. As a consequence, the parameter dm/dt can serve as an index for the magnitude of C if P is determined experimentally or in some other fashion. The differentials dm/dt for different units of homogeneous rock reflect changes of C within rock units and allow one to evaluate the distribution of C in comparable rocks without a preliminary calculation of P.

For the host rocks, where the ore mineralization with higher C values then $C_0$ values is present, an additional branch appears on the hodograph (Fig. Ib) with dm/dt > $(dm/dt)_0$. The second branch forms when t = $T_0$; the further the orebody is from the site of accumulation, the higher the t is. The appearance of a second branch on the hodograph is related to the emergence of ions from the target in quantities which add to the quantity of extracted elements from the adjacent to the site of accumulation rock. Knowing the speed of the ions movement, one can estimate the distance from the site of accumulation to the ore target on the basis of the value for $T_0$.

I.2. The following is the essence of the method of partial extraction of metals.

A prolonged electrical current is passed from an external source through two or more electrodes some of which are equipped as element-receivers (ERs) and positioned on the surface, in boreholes, or in trenches. The quantity of chemical elements accumulating under the influence of the current is determined periodically, and geoelectrochemical hodographs are drawn according to the results of the analysis for each element and each ER. Inferences about the compositions of targets located in the areas of study are made on the basis of the composition of extracted elements. The rates of accumulation dm/dt serve as indices to the composition of elements in the host rocks and in the ores. The variation in dm/dt for different sites of element-receiver placement (the structure of the dm/dt field) reflects the positions of the orebodies in three-dimensional space. The arrival times of the masses of elements from distant targets ($T_0$) characterizes the depth of the target deposition or the distances to the corresponding element-receivers.

I.3. At the present time, three versions of the CHIM method are distinguished: primary, aureole, and logging. The primary version is in the developmental stage. The aureole and logging versions of the CHIM method are discussed below.

Aureole Version of the CHIM Method. In this version, we use the first branch of the hodograph, the one which reflects the extraction of elements from the aureoles of ore deposits. This process occurs in such a way that water-soluble ions are extracted first, then weakly bonded sorbed, then humic-fulvate; further along, poorly soluble carbonates, silicates, and strongly bonded forms of the elements are finally extracted. The portion of water-soluble and other mobile forms relative to the total content of an element is small, several percent or less. Precisely because the trace elements are transported in mobile ionic forms during processes of natural migration, they serve as principal carriers of information about deep-seated mineralizations. When measuring the bulk aureole content of elements (during the soil survey, for example), the information turns out to be within the limits of observational error. This does not allow for discovery of deep-lying targets. On the other hand, when selectively recording water-soluble, mobile forms of element occurrence using the CHIM method, it does become possible to detect ores at appreciable depths.

The usual equipment for the aureole version of CHIM is the following: a system of circular auxillary grounding electrodes of 0.5-1 m diameter with a central primary electrode (ER) which is positioned within the auxillary circular grounding electrode (Fig. 2a) or a ER system with a single auxillary grounding electrode (fig. 2b).

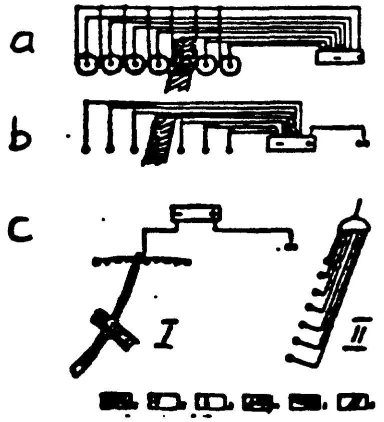

Fig. 2. Diagrams of field apparatus for the CHIM method: a) "aureole" circular; b) "aureole" with common auxillary ground; c) logging (1) general scheme, (P) braid; 1) power source, 2) ER, 3) auxillary electrodes, 4) borehole, 5) projection of ore zones to the surface, 6) orebody.

The extraction of elements proceeds over a certain period of time. In this process, the extracted masses of the elements will be proportional to their contents in the aureole at different points in space. The distributions of extracted masses along profile lines or over areas directly indicate the positions of objects enriched with the corresponding elements. Since the extracted masses characterize the content of elements within an aureole but not within the deep targets themselves, higher quantities of extracted elements still do not allow us to determine the presence of commercial mineralization in the area. This problem will have to be solved by direct physical exploration, and, in the future, by the primary version of the CHIM method.

<u>The Logging Version of the CHIM Method</u>. The small distance between the ER and the borehole wall results in the first branch of the geoelectrochemical hodograph reflecting the extraction of elements from the drilling mud solution; this branch has a small duration along the time axis. With regard to this situation, one can adjust the electric current and the extraction period so that the quantities of elements arriving at the ER correspond, with a small degree of error, to the quantities of these elements extracted from the rocks and ores downhole. These quantities of elements are proportional to the grade of the metals in the ores and rocks. Thus, the extracted masses of elements at different element-receivers placed along borehole walls directly reflect the distribution of grades and allow one to identify ore intervals along axis of the borehole, and to determine the contents of metals in the ores.

The station set-up for logging observations is shown in Fig. 2b The auxillary grounding (iron studs, pipes, etc) are arranged on the surface near the borehole.

I. 4. The CHIM method is designed for:

<u>In the aureole version</u>:

- detection of covered deep-seated orebodies, including targets under a cover of unconsolidated sediments 100-m thick or more;
- exploration on a deposit's margin and tracing of plunging flanks of deposits;
- sorting and verification of geophysical anomalies and defining of the lithology of detected targets.

<u>In the logging version</u>:

- identification and evaluation of ore intervals in the drillholes;
- detection of ore in the vicinity of the borehole.

I. 5. Orebodies of any composition and texture can be explored using the CHIM method. At the present time, positive results have been obtained during explorations for polymetallic, lead-zinc, copper, and copper-nickel deposits. Experience in exploration for gold, tin, and uranium deposits has been limited. The use of the CHIM method for exploration of other types of ore deposits requires trial runs and the development of favorable regimes for electrochemical extraction of the appropriate elements. Appropriate methodologies of analysis of samples from ERs for elements of interest is also needed.

I. 6. The CHIM method in the aureole version can be effectively used during the prospect evalution stage of exploration for deep-seated deposits, including "blind" deposits and deposits covered by unconsolidated sediments of appreciable thickness (100 m or more). The CHIM method results allow one to characterize the metal content of the mineralization and to determine the metal zoning pattern in plan view, including the positions of the upper part ("top") of the mineralization.

Taking into account not only the possibilities associated with the aureole version of the CHIM method but also those associated with other geophysical, geochemical, and geological methods, one can say that using the CHIM version is advisable during the geological mapping of the mining districts on a scale of 1:10,000 or more detailed (usually 1:5,000 - 1:2,000) for:

a) independent detection of deep-seated ores;

b) confirmation of geochemical anomalies defined by the soil surveys and by the method based on modes of elements occurrence (MPF);

c) sorting and verification of geophysical anomalies found by IP, resistivity, and other techniques.

For newly explored territories covered by unconsolidated deposits of appreciable thickness, further exploration of zones discovered by the CHIM method at scales of 1:10,000-1:50,000 will become common practice. This would allow one to confirm the presence of a mineralization, determine locations of the upper portions of the mineralization, and specify more accurately the strike and dip of the ore zones and also the sites of the greatest ore enrichment. It is advisable to drill structural and stratigraphic holes and then deep boreholes at sites determined by CHIM, in order to directly intercept the ore mineralization. The combined use of the CHIM, MPF, and shallow drilling allows one to reduce the amount of heavy exploration work by 40-50% in comparison with exploration of covered areas conducted without the methods named. This method allows one to increase the productivity and lower the expenditures for the area evaluation by a factor of 1.5-2.

I. 7. The CHIM method in the logging version is useful for exploration and surveys. The CHIM results in the logging version for identififying ore intervals and characterizing their metal content allow one to lower the requirements for core recovery when drilling holes in areas with fairly well known lithologic section, and, in many cases, to switch to coreless drilling. Boreholes drilled with a low core recovery or without core can be studied using the standard logging methods in order to divide up the section and to identify ore zones and intervals differing in physical properties. The CHIM surveys are conducted either down the entire borehole or within prospective zones identified by standard logging, to determine the lithology of host rock and content of metals. Study of the entire borehole is necessary if one anticipates the presence of ores indistinguishable from the host rock with respect to physical properties. However, it is more advisable to conduct random sampling of a borehole, since this speeds up the process of studying the borehole and the survey in general.

In the case of an absence of ore intervals or when they are represented by non-commercial mineralization, the boreholes can be declared barren on the basis the CHIM results. Ore intervals established according to CHIM data are usually traversed by a second borehole of limited length (usually a few tens of meters) with complete core recovery for verification and laboratory assaying of ore components. Shortening drilling time as a result of lowering the requirements for core recovery or proceeding with coreless drilling leads to an increase in productivity and a lowering of the cost of direct physical exploration by 12-15%.

## 2. EQUIPMENT FOR THE CHIM-10 STATION

### 2. 1. Purpose and Design

2. I. I. The purpose of the CHIM-10 equipment is to induce and to record electrochemical processes by extracting chemical elements from rocks and ores in order to discover covered deep-seated ore deposits from the surface or by drilling at the same time gathering information regarding the composition and location of the mineralization.

2. I. 2. Included in the CHIM-10 station are: a diesel-electric alternating current assembly, the station control panel (including a converter of alternating current to direct, and a group of measuring-regulating units), a chemical laboratory with appropriate equipment for conducting chemical analyses, and stationary and auxillary instrumentation, tools and supplies (element-receivers, cables, leads, reels, etc).

2. I. 3. The diesel-electric alternating-current assembly ESD-10-VS/230M is mounted on a TAPZ-755 single-axle trailer. The rest of the instrumentation and equipment is housed in a CGK-7L truckbed of a ZIL-131 truck. The truckbed was divided into two parts by a solid partition. The chemical laboratory is set up in the front portion and the equipment unit is set up in the rear portion. The compartments for the chemical laboratory and for the equipment unit have their own entrance doors.

2. I. 4. In the equipment unit, we set up a control panel on a carcass stand. Rectifiers are positioned on both sides of the control panel; control units assemblied on printing plates are arranged above the rectifiers. Measuring-regulatory units connected with the rest of the station set-up by means of pin connections are placed in the middle part of the console. A TS-10 power transformer is installed in the lower-middle part of the console. Control units and indicator lights are located on the face panels of different units complete with labels.

A work table and a bench with drawers for stationary and auxillary instrumentation are installed along the walls of the equipment unit compartment.

A light panel is fixed to the left upper portion of the front wall of the equipment unit; on the panel, there is a voltmeter for monitoring the voltage of the system, switches, 220-V and 12-V outlets, and cut-off fuses. Work tools (axe, saw, shovel, etc) are hung on the door in the back of the truck bed.

2. I. 5. The following are installed in the chemical laboratory: an exhaust cabinet with an electric heater, a work table with drawers, a pedestal with a sink for pouring out

solutions, and a bench. The fume cabinet is connected to an exhaust apparatus installed on the outside, over the cabin of the truck. An exhaust apparatus switches on a type TS4-70 centrifugal ventilator with an AOL12-I4 electric motor. The capacity of the exhaust apparatus is 600 m³ of air per hour.

The electric heater, intended for evaporating solutions, consists of three PE 800/3-5 electric hot plates. The electric heater, the exhaust apparatus, and the lights are connected up with the system via switches on a switchboard attached to the upper part of the wall above the work table.

Equipment for chemical analysis of the samples (a FPL-I polarograph, a PEC-56 photoelectric colorimeter, and chemical glassware) are arranged in the drawers under the bench, the lower portion of the fume cabinet, and in the desk drawers.

2.I.6. The input panel is located in a hatch on the left wall of the truck bed. There are pintles on the panel: connectors for joining up with the electrode-grounds, a pin connector for connecting into the diesel-electric assembly, and also a terminal to join up with the protective grounding of the station. During operation and transport of the station, the hatch to the input panel is covered with a lid; a blocking device which turns off energy transmission from the diesel assembly if the lid to the hatch is not closed is simultaneously turned on.

2.I.7. A structural diagram of the CHIM-10 station is shown in Fig. 3; a functional electrical diagram is shown in Fig. 4.

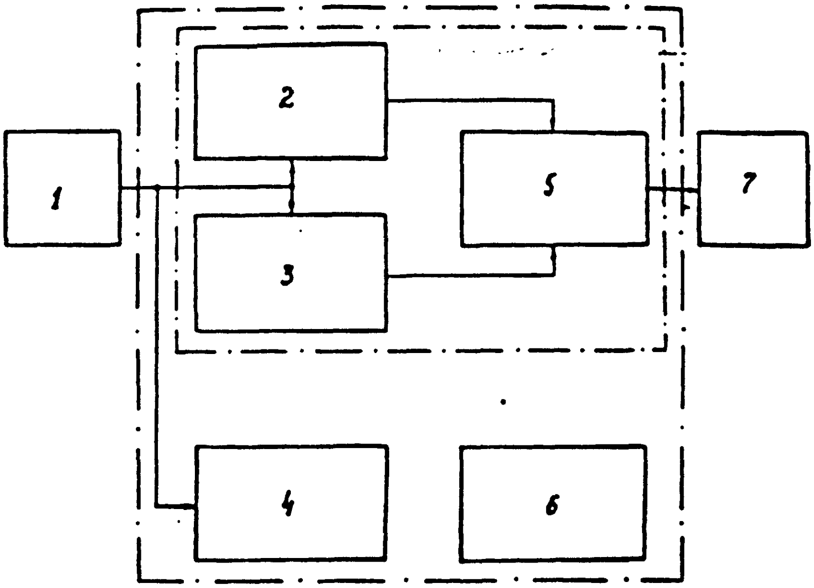

Fig. 3. Structural diagram of the CHIM-10 station:
1)diesel-electric assembly, 2 and 3) converters of AC voltage to direct; 4) chemical laboratory; 5) measuring-regulatory units; 6) auxiliary equipment; 7) stationary equipment.

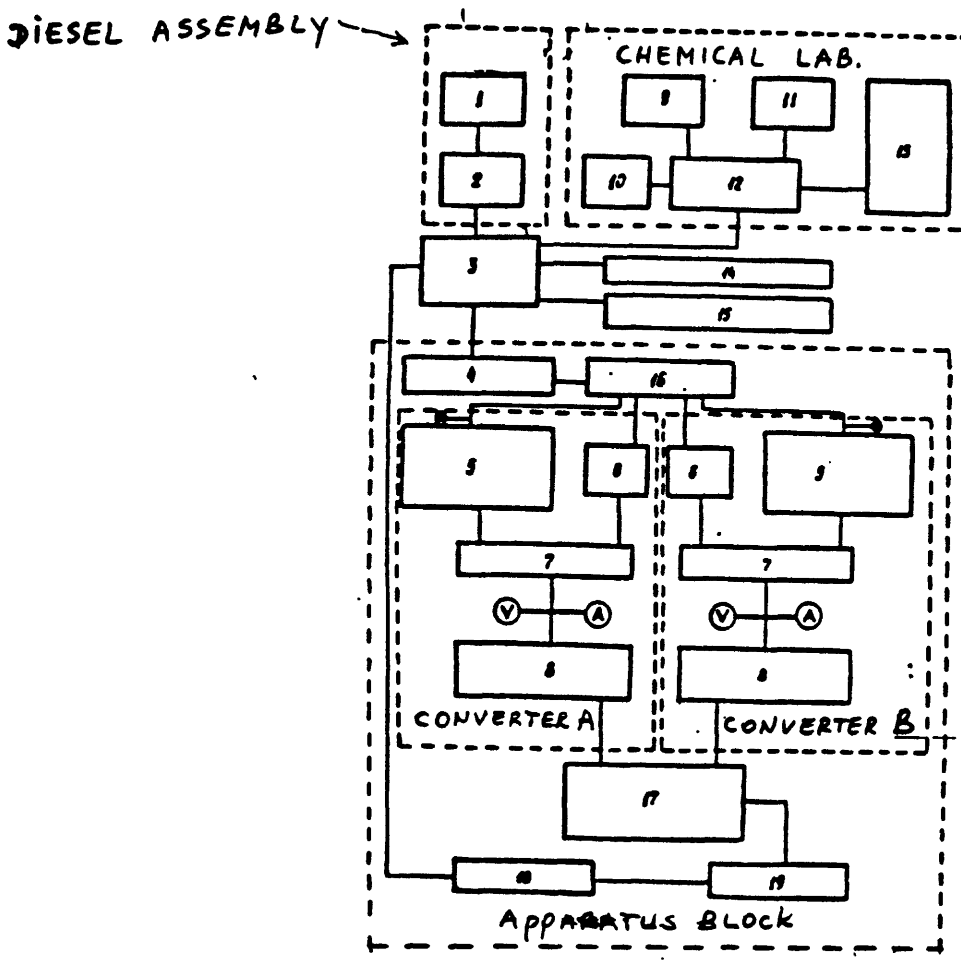

Fig. 4. Functional electrical diagram of the CHIM-10 station: 1) diesel-electric assembly, 2) precautionary disconnecting contactor, 3) input panel, 4) switches, 5) rectifier control unit, 6) switches, 7) rectifiers, 8) power switches, 9) FPL-1 field polarograph, 10) electric hot-plate, 11) PEC-58M photoelectric colorimeter, 12) distribution panel, 13) electric motor for exhaust apparatus, 14) element-receivers, 15) auxillary grounding electrode, 18) power transformer, 17) distribution plate, 18) unit of ballast resistors, 19) unit of shunts.

From the diesel-electric assembly (I) (Fig. 4), a three-phase variable voltage arrives at input panel (3) through the precautionary disconnecting contactor (2) and, further along, arrives through a power transformer to ac-dc converters (A and B) consisting of control unit (5) and rectifiers (7). DC voltage which could be set with the aid of the control units to any magnitude from 0 to 500 V (for each converter independently), arrives from the outputs of the converters at distributing board (17) of the control console. The dc voltage at board (17) is transmitted over four channels to shunt unit 19, where each channel branches into seven circuits switching shunts for measuring of the current flow through the corresponding circuit. Each circuit passes through unit 18 consisting of ballast resistances making it possible to regulate the current in the circuit. From this unit, the voltage arrives through the input panel to the system of surface or borehole electrodes.

## 2.2. The Power Generator

2.2.I. The power source for the CHIM-10 station is the generator of the ESD-10-VS/230 alternating-current diesel-electric assembly; it has a power of 10 kw and produces a three-phase current with a voltage of 230 V and a frequency of 50 Hz. A transformer and a contactor with an auxiliary rectifier designed for precautionary disconnection of the power grid when the blocking switch on the output board and in the control console is activated, is set up within the protective casing of the assembly.

2.2.2. A type TZ-10 power transformer was used to increase the voltage arriving from the electrostation to the converters A and B. The latter convert ac voltage to dc voltage, which can be regulated by potentiometers that are located on the control panels.

The power component of the rectifiers is based on a Larionov bridge circuit (Fig. 5). The control valves in it (diodes-thyristors of TL-2-100 type) are used only in the $D_4$-$D_6$ cathode group. The anode group is assembled on uncontrolled $D_1$-$D_3$ valves (type VL-100 diodes). Commutation of current in the cathode group ($D_4$-$D_6$) occurs at the moment of transmission of controlling pulses to the appropriate units. Commutation of current in the anode group ($D_1$-$D_3$) occurs at the moment when the valves are spontaneously opened.

A special feature of the scheme under consideration is the use of a zero diode $D_0$ designed to prevent the overvoltage on diodes $D_1$-$D_6$ under the inductive load.

In order to regulate the current in the supply circuits, we made use of a property of thyristors; they conduct current after transmission of a current pulse to a control electrode when there is a positive potential at the anode of the thyristor. The thyristor does not conduct current if a voltage with negative polarity is applied to its anode. The thyristor restores its non-conductive properties only after the cessation of current flow through it. In accordance with this, the current in the load of a three-phase bridge flows only at those moments when the corresponding thyristor of the bridge is open.

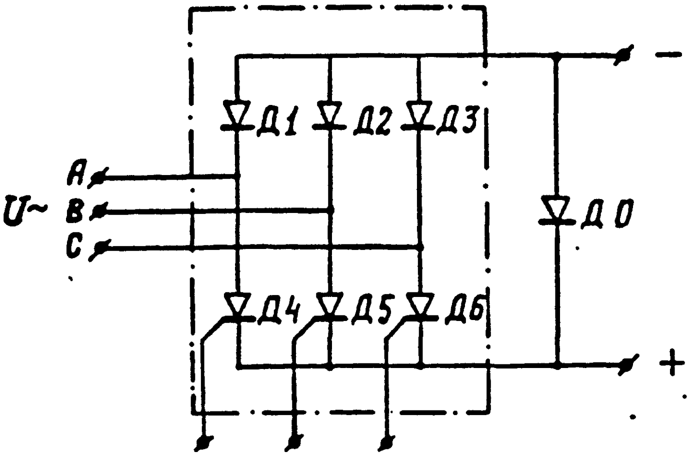

Fig. 5. Larionov circuit for rectification of alternating current.

2.2.3. The time-pulse method of controlling current in the load consists in the fact that a positive pulse is provided to the control electrode of the thyristor at the moment $t_2$ (Fig. 6), as a result of which the thyristor becomes conductive and the current in the load flows.

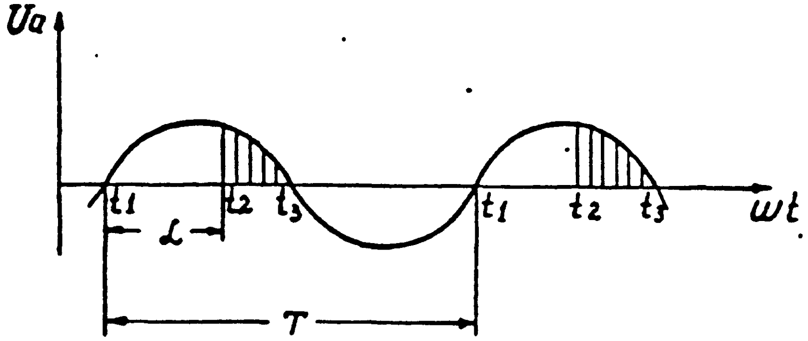

Fig. 6. Illustration of principle of control by output voltages from rectifiers.

By changing the time moment $t_2$ between $t_1$ and $t_3$, i. e., by changing the regulation angle $L = wt_2 - wt_1$ from zero to 180 electrical degrees, one can regulate the flow in the load from $I = I_Н$ to $I = 0$. Attention should be given to the fact that a smaller control angle corresponds to a larger current in the load.

A functional diagram of a control system using thyristors is presented in Fig. 7. Control pulses are formed according to the vertical control principle. In order to implement the latter, a reference saw-toothed voltage is created and compared with the control voltage; the comparison scheme generates a small-amplitude pulse amplified by a dual-cascade amplifier at the moment the voltages being compared are matched. The pulse is then differentiated and arrives at an amplifier designed to form a control pulse with the given parameters. The formed pulse then gets to a power amplifier and passes through a protective network to the control electrode of the thyristor.

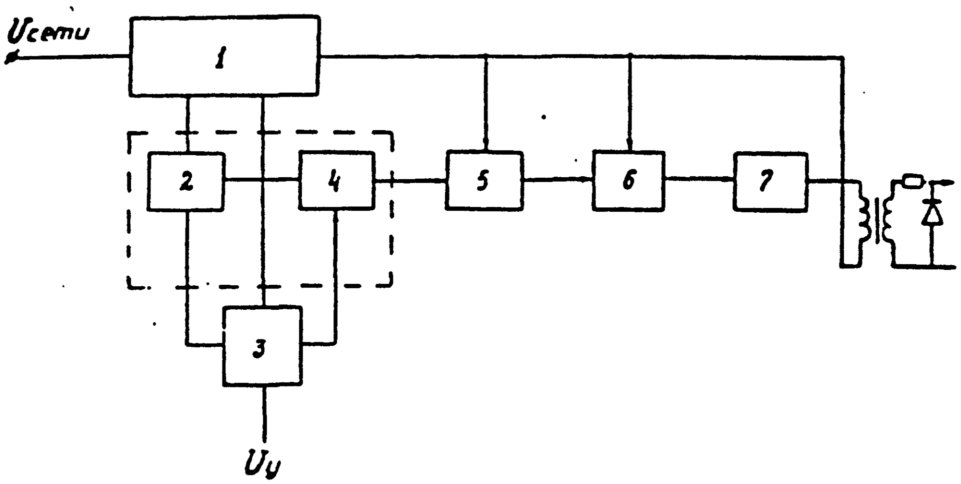

Fig. 7. Functional diagram of formation of control impulses: 1) stabilized rectifier; 2) saw-tooth voltage generator; 3) phase shift control unit; 4) comparison scheme (curcuit); 5) voltage amplifier; 6) generator; 7) power amplifier.

If the control voltage $V_{c1}$ is small, the reference voltage rapidly reaches the level of the control voltage and a pulse corresponding to the control angle $L_1$ is generated. When there is an increase in the control voltage to a value $V_{c2}$, the reference voltage will increase further, until the moment of matching of the two voltages occurs, when the pulse corresponding to the control angle $L_2 > L_2$ is generated. By selecting boundary values for the control voltages $V_{c1}$ and $V_{c2}$ and the steepness of rise at the front of the saw-toothed reference voltage, it is possible to set the values $L_1 = 0$ and $L_2 = 180°$; this corresponds to the changes in the load current from $J_H$ to zero when there is a change in the control voltage from $V_{c1}$ to $V_{c2}$.

A diagram using thyristors to obtain saw-toothed voltage for one of the three channels present in the control system is shown in Fig. 6, a. The saw-toothed voltage is formed on C1 by a charge through resistors R6 and R9 from a high-voltage, stabilized supply source. The C1 charges according to the exponential law, therefore, the initial "rectilinear" area of the charge is used in the diagram of saw-tooth voltage generator. Its rectilinearity is ensured by the selection of the voltage for the source and by the large time constant for the circuit. The initation of the charge of the capacitor and its discharge after the formation of the saw-toothed voltage are controlled by a diode commutator. Graphs of voltages on Fig.8,b depict the operation of the commutator.

Diodes D10 and D1 are connected in parallel to capacitor C1. When the diode D10 is blocked, C1 is charged and a front of saw-toothed voltage is formed. If diode D10 is in the conductive state, the capacitor is discharged through this diode, the resistor R2, and the coil of a two-phase (2p) transformer.

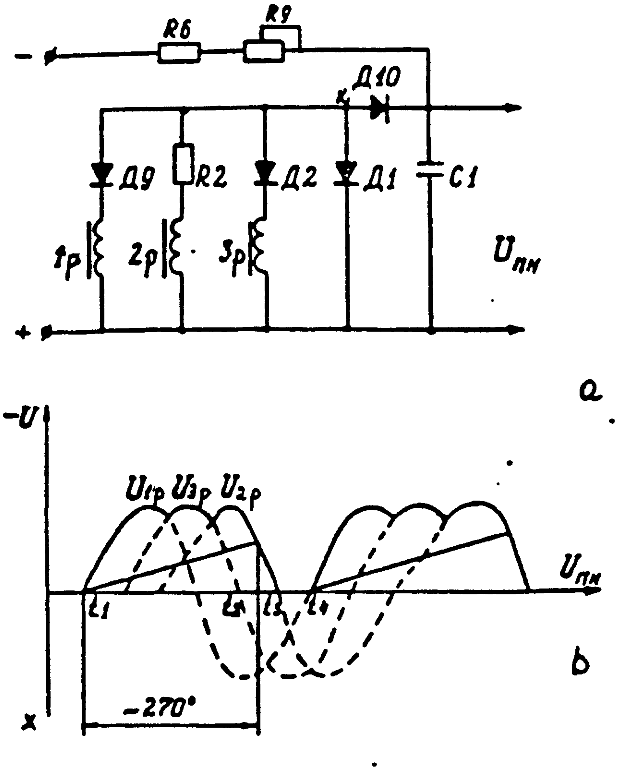

Fig. 8. Circuit for obtaining saw-toothed voltage: a) main circuit; b) graph of voltages.

At the moment $t_1$, the voltage of phase Ip with a negative polarity is applied through diode D9 to the point "K," as a result of which diodes D1 and D10 become blocked and the formation of a front of saw-toothed voltage strictly synchronized with the voltage of phase Ip begins. The negative voltage at the point "K" is subsequently maintained by the oppositely phased voltage of phase 3p and the voltage of phase 2p (through resistor R2). At the moment $t_2$, the saw-toothed voltage becomes equal to the voltage of phase 2p, diode D10 is opened, the charge of the capacitance of C1 is terminated, and the current from the supply source flows along the circuits of R6, R9, diode D10, R2, and the coil of the transformer. The capacitance C1 is discharged by way of a RC-circuit: diode D10, R2, and the coil of the transformer. The voltage on the capacitance cannot be altered more rapidly than the voltage of phase 2p, since diodes D9 and D2 are blocked by the positive charges of the corresponding phases. The current in the circuit transformer coil, R2, and diode D1 is set up by the greater than the charging current; therefore, diode D1 and D10 remain open from the moment $t_3$ to the moment $t_4$; their resistance has a small value in this case, and the voltage on the capacitance during this period remains equal to zero. From the moment $t_4$, the process is repeated in the same sequence as from the moment $t_1$. The forms of the phase voltages will have no qualitative effect on the formation of the saw-toothed voltage if the phase voltages are always greater than the voltage being created.

The inputs of the SA1+SA3 surge amplifiers (Fig. 9) connect into the C1+C3 capacitors through a comparison circuit realized at the D13+D15 diodes. The moment for activating the comparison circuit is determined by the voltage $V_c$ arriving from a direct-current amplifier (T1+T3 transistors) through resistors R12+R14. When the voltage on the capacitors C1+C3 reaches the value $V_c$, diodes D13+D15 are opened and the voltage from capacitors C1+C3 arrives at the base of the transistor T1 of the surge amplifier, with transistor T1 opening and transistor T2 closing as a result. At the moment transistor T2 closes, a negative pulse which opens the transformer amplifier at transistor T3 is activated at resistor R5 of the RC differentiating circuit C3 and R5. Diodes D3 and D5 serve as a "clip" of a mid-portion of the differentiated pulse with a duration of 80+100 msec.

The power amplifier function is performed by transistor T4, and diodes D7 and D8 serve to protect the control electrodes of thyristors from overshoots of large voltages with negative polarities.

The supply source is realized by diodes D22+D26 and the power source of the surge amplifiers SA1+SA3 is realized by diodes D28+D31.

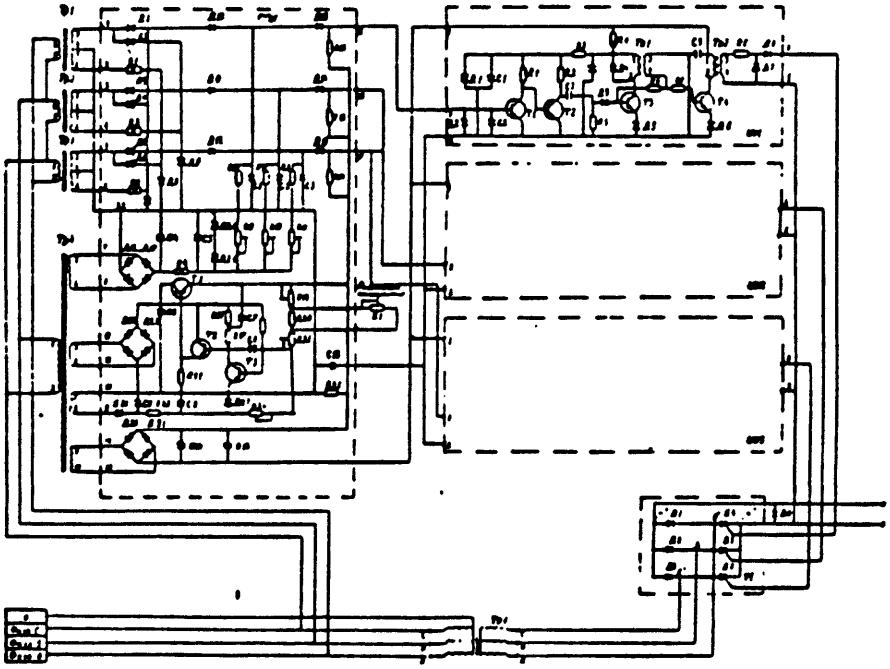

Fig. 9. Main circuit of control console.

## 2.3. Current Control Console, Element-Receivers, and Measuring Instruments.

2.3.1. The distribution board of the control console was designed to distribute current arriving from the outputs of ac-dc converters along four channels. A unit of shunts serves to divide each of the four channels into seven identical circuits along which voltage is transmitted to 28 element-receivers (ER) and serves to control currents in the circuits of the element-receivers.

The unit of ballast resistors contains 168 active resistors. It is possible to use from one to six ballast resistors within the circuit of each element-receiver.

2.3.2. The system of surface and borehole electrodes permits the use of 28 element-receivers (ERs), each of which is part of an autonomous current loop, and a common grounding electrode, the anode. The ER and the auxillary ground are included in the make-up of the stationary installation. Also included in this installation are: power cables, cables of the blocking system, a telephone lead, four cables which are braids 130 m in length each for connecting up with the ER, and four cables which are extension braids with lengths of 150 m. Fifty-six surface element-receivers, pins for the auxillary ground, and a cable for connecting the instrumentation bank to the logging-hoist collector for borehole studies are included in the standard inventory of the CHIM-10 station. The braids and extensions are made out of GPSMPO wire. Each braid has a pin connection for joining into the instrumentation bank and seven bipolar branches for joining with the grounds and element-receivers. The branches are arranged at a distance of 20 m from one another. There are no branches for the cable-extensions, and they are used when assembling the supply circuits for the surface electrodes. Their arrangement at the site depends upon the position of the station relative to the surface electrodes. The connection of the electrodes to the branches of the braided cable is carried out with the aid of connective wires with single-contact pin connections.

One should adhere to a specific system when connecting the braids to the input board. Each of the four braids contains 7 branches for hook-up to the element-receivers. The latter are numbered in accordance with their position on the terrain in such a way that they create a series of integers 1, 2, 3, etc. when a profile is passed from one end to the other.

Since the CHIM-10 station can be positioned on the profile arbitrarily in relation to the ER (closer or at the other end, or in the middle of the profile), the ER can be numbered either from the tip of the braided cable close to the station or from the far cable.

In order to prevent errors when connecting a braid to the input board, there are two pins for each braided cable (fig. 10) designated by the 1st numbered ER within the braid in forward and reverse order (for example, 1+7; 7+1 or 8+14; 14+8, etc.). The braids are designated by the highest and lowest ER enumerations written in order of the distribution from the pin (from the input board) to the end of the braid and are connected with the pin of the input board with a designation coinciding with the designation of the braid (for example, braid 14+8 is connected to pin 14+8 but not with pin 8+14).

The cables are wound on portable reels for transport and protection; the ERs are packed away in special boxes.

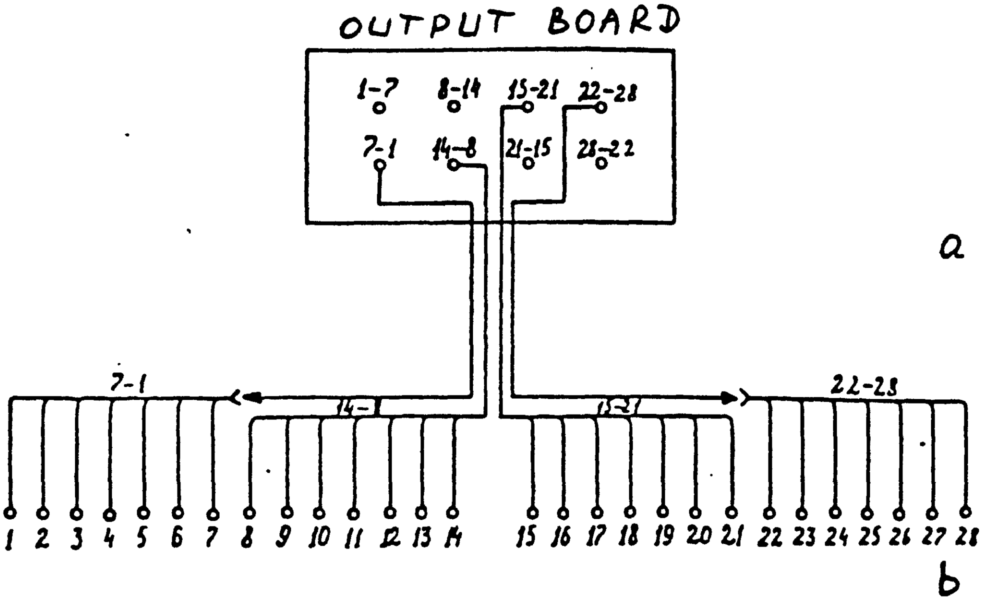

Fig. 10. Example of connecting braids with output board: a) numeration of pins, b) numeration of ER circuits.

2.3.3. An element-receiver for surface studies (Fig. II) is a cylindrical polyethylene vessel with a capacity of 40+50 ml and possessing a porous membrane made from parchment (GOST 1341-60). The metallic electrode-rod of the element-receiver is made from type VTI-0 titanium. For borehole studies, an element-receiver in the form of a glass made of porous ceramic is used. Its casing has a volume of approximately 100 ml and functions as a membrane. The ceramic glass is placed in a protective perforated jacket of polyethylene. It is secured to the cable with an adhesive tape. The appropriate wire in the cable is secured to the head of the ER, adhering to all measures needed for hermetization of the joints, thus making operation in boreholes possible. The head of the ER should tightly but not hermetically cover the mouth of the ceramic glass. The designs of the contact and the cap are identical for surface and borehole ERs.

2.3.4. A voltmeter for measuring the voltage in the supply circuit within a 0-500 V range of measurement for direct current is installed on the front panel of the control console along with an ammeter for measuring current of up to 30 A in the load. Bulbs signalling the transmission of voltage through all of the circuits of the converter are placed beside the control instrumentation.

Switches for "power-circuits" and "control-circuits" designed to turn on converters are installed on the front panel of the control console.

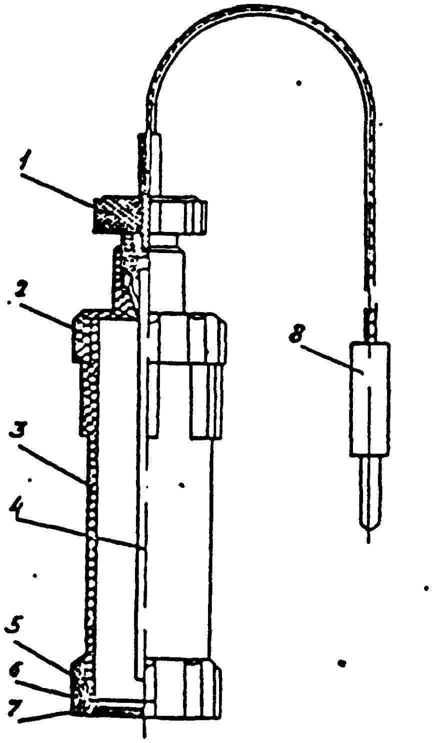

Fig. 11. Element-receiver for surface monitoring: 1) contact; 2) cap; 3) cylinder; 4) titanium electrode; 5) nut; 6) washer; 7) membrane; 8) single-pin plug.

The outputs of the rectifiers are connected to the circuits of the element-receivers through two-way "element-receiver-polarity" switches. The two-way switches are designed for measuring the polarity of the output voltage of a rectifier when the station is operated under a regime of element-receiver depolarization. The positions of the two-way switches should be identical for all regimes of station operation. If not, the voltage from the rectifiers will not arrive at the output, in view of their mutual blocking. An active resistor, a shunt, is included in the circuit of each element-receiver for control of the load currents. The fall in voltage at the shunt is proportional to the current in the load and can be measured with the aid of a measuring instrument. The MI1 measuring instrument is connected to the shunts through two-way switches. The hook-up circuit for the IP1 instrument is realized in such a way that an instrument can be connected only to a single shunt, the two-way switches for which, other than the one used for measuring, should always be located at position "1."

The current in the ER circuits can be measured within two boundaries: 0+1 A and 0+0.25 A. The limits of measurement are set by means of a "range" tumbler switch. There are trimming resistors for the calibration of the measuring instrument. The current at different polarities can be measured with a MI-1 probe by switching on a "polarity" tumbler switch. From one to six ballast resistors can be turned on or disconnected in the circuit of each element-receiver with the aid of two-way switches.

The necessary current in the circuit of each ER can be found by selecting a value for the ballast resistance and the necessary voltage at the output converters A and B. The intensity of the electrical field around each of the ERs is measured with the aid of a V7-15 high-resistance voltmeter and two titanium electrodes mounted on an extension plug and arranged at distances of 10 cm from one another.

2.3.5. The measuring instruments of the CHIM-10 station are designed for control of the technical state and operational regime of the station and also for carrying out analyses in the chemical laboratory.

The technical state of the station is monitored by a complex instrument TS4315, a 4100/3 megometer, 500 V, 500 MOhm, and a V7-15 voltmeter.

Voltmeters installed in the control console and also a V7-15 voltmeter are used to monitor the operational regime of the station. A FPL-1 polarograph for field laboratories and a PEC-56M photoelectrocolorimeter are used in the chemical laboratory.

2.3.6. The listed equipment, with the exception of the FPL-1 polarograph, is part of a standard measuring equipment widely used in various areas of research, including geological and geophysical investigations. This equipment is described in many instructional manuals and will not be given special consideration here. The FPL-1 polarograph was designed for determining quantities of chemical elements in samples of solutions from element-receivers during operations using the CHIM method.

## 2.4. The FPL-1 Polarograph

2.4.1. Operations with the FPL-1 polarograph consist of the following. Solutions of samples from the ERs are placed in electrolytic cells in which a working electrode, a reference electrode, and an auxiliary electrode forming a polarization current with the working electrode are present.

The next system of equipment maintains a fixed voltage on the working electrode by varying the polarization current. Simultaneously, this system allows one to change the voltage of the working electrode in a linear fashion to the positive or negative side from the established value. The polarization current is recorded during the process of varying the voltage of the working electrode. The curve of the dependence of the polarization current upon the electrode voltage carries information concerning the nature of the elements in the sample and their concentrations.

The analysis of the samples consists in the following stages: stirring of the solution, cathode precipitation of the metals on a solid graphite electrode, calming of the solution, and dissolving of the precipitated components along with recording of the dissolution currents. The order of stages in the analysis is facilitated by the automatic shift of operational regimes in the polarograph.

Included in the polarograph (Fig. 12) are: a generator of "beat" impulses; a 1:32 divider; a converter of code to saw-toothed voltage; a plate of regimes; switch junctions for the following regimes: first exposure; stirring; precipitation; second exposure; build-up; branch-points to set up amplitudes of build-up voltage and precipitation voltage; amplifiers of the polarization current, and recorded current; an "auto-manual" two-way switch, and a power supply unit.

In the automatic control regime, the polarograph operates in the following fashion. When the "cycle" button is pressed, the first exposure branch-point is turned on and the mechanical agitator is turned on simultaneously. The "mixing" indicator light on the front panel lights up. After the end of the first exposure, the build-up branch-point is turned on along with the tape mechanism of the recorder, and the "build-up" indicator light on the front panel lights up. The build-up can be stopped when desired by turning the "stop-build-up" tumbler switch. In this case, the "stop-build-up" indicator bulb lights up. When the "stop-build-up" tumbler switch is turned off, the indicator light dies down and the build-up continues.

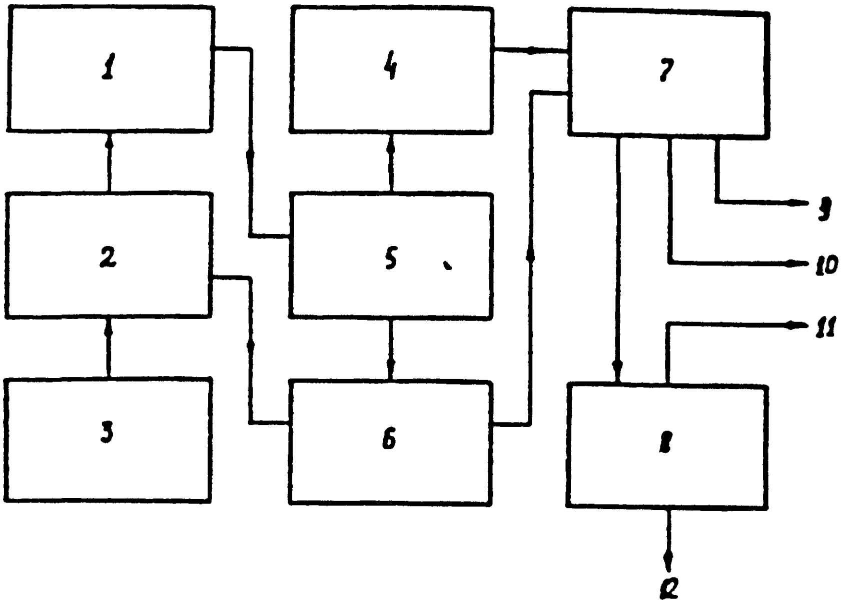

Fig. 12. Block Diagram of FPL-1: 1) converter of code to saw-toothed voltage; 2) "beat" impulse generator and automatic device for switching on exposure, precipitation, and build-up regimes; 3) power supply unit; 4 and 5) branch-points that set up precipitation voltage and amplitude of build-up voltage, 6) branch-point for switch of build-up regime, 7 and 8) amplifiers of polarization current and recorded current. Branches to electrodes: 9) reference, 10) working, 11) auxillary, 12) branch to recorder.

At the end of a selected time of build-up, the monitoring system returns to the original state.

In order to change to a manual regime of polarograph operation, it is necessary to place the "auto-manual" two-way switch in the "manual" position and switch on the required regimes with the aid of the corresponding tumbler switches and the "build-up" button.

2.4.2. The working order of the FPL-1 polarograph can be checked in the following fashion. Prior to transmission of the supply voltage to the polarograph, the control units should be set at their original positions (see TABLE 1)

TABLE 1

| Control Units | Original Position |
|---|---|
| "network" | "off" |
| "instrument dial" | 20 V |
| "regime" | "manual" |
| "mixing" | "off" |
| "precipitation" | "off" |
| "build-up" | "off" |
| "recorder" | "1000" |

The positions of the remaining control units are arbitrary. Next, one should connect the recorder, agitator, and an equivalent electrolytic cell to the polarograph. The recorder and the corresponding operational regime for the amplifier of the supply unit should be switched to the "250 mV" range of measurement; also, all tasks concerned with preparing the recorder for operation according to the maintenance manual should be carried out.

In the equivalent electrolytic cell, we set $R_c$ = 500 kOhm, $R_p$ = 100 Ohm.

We then check:

a) the change in the set polarizing voltage, for which two-way switches labeled "precipitation" and "potential" can be set at various values; on the scale of the instrument showing the voltages at the working and auxiliary electrodes, we monitor the voltage and make sure it remains at the set value. This monitoring is done with the tumbler switch in positions marked "precipitation"-"polarity" "+" and "-";

b) the shift of zero on the recorder. While turning the knob labeled "pen"-"shift," we monitor a shift of the recorder pen when the knob is moved from one extreme position to the other; the recording pen should move over the entire width of the scale;

c) the manual control of the analysis regime and light signalization. By setting the two-way switch for the regimes in the "manual" position and the "precipitation potential" two-way switch at position 0.3, we sequentially turn on the "agitation," "precipitation," "build-up," "stop build-up," tumbler switches and positively check· all of the activated regimes, the lighting-up of the corresponding indicator bulbs, movement of the chart strip during the "build-up" regime, and rotation of the electrode in the "agitation" regime;

d) the change in the polarization current. By setting the two-way switch for "recorder mA" at position 100, we change the position of the two-way switch "precipitation"-"potential" from 0 to 0.5 V and check a corresponding shift of the recorder pen; this indicates a change in the polarization current.

e) the automatic control of the analysis regimes; for which, by setting the two-way switch for the regimes to the position "auto", and the two-way switches for "precipitation"-"potential" to the position 0.5, for "polarity"-precipitation" to position "-", "min. precipitation" to position 1, "build-up"-"polarity" to position "+", "min. build-up" to position 1, "build-up - amplitude" to position 1.0, and "recorder mA" at position 500, and by pressing the "cycle" button, we switch on agitation and check the correctness of the alternation of analysis regimes.

## 2.5. Technical data and check of the technical condition of a CHIM-10 station

2.5.1. Basic technical information on the CHIM-10 station:

| | |
|---|---|
| Power of electrical energy source | 10 kw |
| Nominal voltage | 230 V |
| Current | triple-phase (50 Hz) |
| Voltage of direct current in the load | 0+500 V |
| Current strength | 0+20 A |
| Number of channels to element-receivers | 28 |

The current in the circuit of each element-receiver can be varied either smoothly, by regulating the voltage at the converter output, or in a step-wise fashion by switching of the ballast resistors. The current is measured without a break in the current circuit.

A chemical laboratory enabling us to perform chemical analyses of the solutions from the ERs at the immediate site of station operation (profile, borehole) is included in the station.

2.5.2. A summary of the basic checks of the condition of the CHIM-10 stations presented in TABLE 2.

TABLE 2

| Necessary to Check | Technical Requirements |
|---|---|
| 1. Technical state of the diesel-electric assembly | Technical state should correspond to the requirements in the manual for maintenance of the diesel-electric assembly. |
| 2. Resistance of the insulation on the input and output cables relative to the frame (using megohmmeter connected to the grounding terminal and the one on connecting panel) | The resistance of the insulation should be no less than 100 M , and no less than 10 M for elevated humidity. |
| 3. Strength of connections of units, contacts at power curcuits and control curcuits | Bolts and nuts, with the aid of which the connections are secured; units and contacts should be well secured. |
| 4. All station units (external inspection) | There should be no visible damage to units and no extraneous objects on their working areas. |
| 5. Stationary equipment (external inspection) | There should be good insulation without visible damage, reliable connections. |
| 6. Operation of station with hook-up to equivalent load (1-2 kw) | Voltage should smoothly vary from 0 to 500 V when the position of the potentiometer knob "Voltage Control" is changed. |
| 7. Resistance of insulation of power users in the chemical laboratory (megohmmeter connected) | Resistance of insulation should be no less than 10 Mohm under normal conditions and no less than 1 Mohm in conditions of high humidity |
| 8. Operation of equipment in chemical laboratory | Ventilator motor in exhaust cabinet should operate noiselessly and without vibration. Electroplates should be heated for no more than 10 minutes and during their operation there should be no sparking on contacts. The FPL-1 polarograph should be operative. |

# FIELD OPERATIONS

## 3.1. Operational Sequence. Arrangement of station and electrodes.

3.1.1. For investigations using the CHIM method in the aureole version, the station is first set up at the site and then braided cables are laid out from the station along a given profile. The element-receivers and auxiliary grounding electrodes are then laid out. The ERs are filled with the working solution, the grounding electrodes are connected to the braids, and the latter are connected to the station. The electrical regime for extracting the elements is then set by selecting the current through each element-receiver which will provide the desired voltage around the ER. After this, electrochemical extraction takes place over a fixed time period during one or several cycles. After each cycle, samples of solutions are removed from the element-receivers and transferred to the station's chemical laboratory for analysis. The ERs are filled with new working solution in order to continue the extraction process. After the last cycle of the ERs, the grounding electrodes and braided cables are removed from the profile and secured within the station for transport. The station is then moved to a new site of operations.

During the extraction process, an analysis of the solution samples from the element-receivers is performed in the laboratory and the element-receivers are treated and prepared for new observations. Working solutions, auxiliary reagents, glassware, etc. are also prepared for further work. A certain amount of the prepwork is performed at the base camp prior to departure for the field.

For investigations using the CHIM method in the logging version, laying out the cable and spacing ERs at the site are replaced by hoisting operations down the studied borehole using a logging hoist with a special cable wound around the winch. ERs are attached to this cable.

3.1.2. Observations using CHIM in the aureole version are conducted along an earlier developed survey grid. Station sites are marked in accordance with the dimensions and geometry of the given area, and then braided cables are laid out with branches for connection with the element-receivers. Usually the station is set up in the center of the profile and two braided cables (14 element-receivers 20 meters from each other, 260-280 meters total) are laid down to one side of the profile while the remaining two braids are laid down to the other side. In some cases, it is convenient to position the station so that three braided cables (21 ERs at a distance of 420 m) are located on one side of the station, and a single braided cable (7 ERs at a distance of 140 m) is positioned in the other direction.

The length of the braided cable allows one to move the station away from the profile line by a distance of up to 20-40 m. When locating equipment in this manner, suitable sites are selected for positioning the station along with the diesel assembly so that the latter is located on the downwind side of the station and camp. The station and diesel assembly are positioned in the same manner for logging observations. The station and the diesel assembly are connected to one another by a special cable.

3.1.3. The braided cables and their extensions are positioned from the station along the profile. Branches from the braids allow each element-receiver to be positioned within a radius of 3 m. When selecting a site for setting up an element-receiver, the following requirements should be met:

a) absence of contaminants associated with industrial waste;
b) absence of boulders, coarse rock debries, and root stalks;
c) the area should be level and should exclude the possibility of rain flooding and contamination by debries;
d) all of the ERs on the profile and within the area should be set up in the same soil horizon; the topmost humus layer $A_1$ and the clay-rich horizon B are most suitable for this.

It is recommended that ERs prepared for set up and filled with distilled water be transferred to their set-up sites in containers. Each element-receiver should be set up in the following fashion. A blade with a broad cutting edge is used to dig a hole in the soil 15-20 cm in diameter and to the depth of the soil layer desired (often 5-20 cm). Water from the ER is poured into the hole. After the soaking the soil with water, the ER is inserted into the hole, the hole filled from the sides one third of the way with earth taken from the hole earlier, then the soil is compacted. Then a certain acidic solution (the kind and concentration of which is discussed below) is poured into the element-receiver. The acidic solution is poured with enough to ensure that it does not fall on the ground around the ER. The filled element-receiver is covered by a cap with an inserted titanium electrode. A lead passing through the protective cap of the ER is joined to a branch of the braid by a uni-polar plug.

When setting up the element-receivers, we make a diagram of their positions and note elements of relief, intermittent streams, roads, areas with crops, etc. In addition, we indicate the composition and changes in the soil content, the soil texture, humidity, and other characteristics.

For a general evaluation of the soil properties at individual points along the profile, we measure resistivity with the aid of a four-terminal installation (AB = 60 cm, MN = 10 cm) prior to setting up the ERs.

3.1.4. The acidic solution in the element-receiver serves to prevent alkalization of the surrounding environment and facilitates the accumulation of metallic cations at the ER. Nitric acid, the anion of which forms easily dissolved compounds with the majority of extracted metals, should be used.

In order to prevent alkalization of the ER during the extraction cycle, it is necessary that the pH of the solution not exceed the pH for hydrate formation with respect to the extracted metals. Therefore, the original acidic solution should either have a sufficient quantity of hydrogen ions for discharge during the electrode reaction, or the $OH^-$ ions, forming during the dissociation of water when electrical current passes through the ER, must be systematically neutralized in the solution.

The concentration of the solution can be calculated according to the formula:

$$C_{sol} \cong \frac{K \cdot I \cdot T}{V \cdot n} \qquad (3)$$

where K is the electrochemical equivalent of the hydrogen ions, equalling 0.037 g/A-hr; V is the volume of the element-receiver in liters; n is the basicity of the acid[*]; t is the time for the cycle in hours; and I is the current passing through the ER in A.

According to the experience of previous operations, the current amounts to hundreds-tens of amperes in the aureole version and amounts to tens or less than ten amperes for logging measurements.

The concentrated acid is diluted with distilled water in order to prepare the required solutions. Concentrated nitric acid has a normality of 14. In order to prepare one normal (1 N) solution, the nitric acid is diluted by a factor of 14, i. e., 1/14th liter of the acid is dissolved in 1 liter of distilled water (1 to 1/14). To obtain a 2 N solution, the acid is diluted by a factor of 7 (14/2); 2/14th (1/7) liter of acid is dissolved in one liter of distilled water (1-1/7).

3.1.5. For logging observations, specially constructed element-receivers are connected with strands of multi-conductor cable. Probes with outlets arranged at the spacing of the ER array are usually made from lengths of cable. Probes that are

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[*] Nitric acid ($HNO_3$) n = 1

used most often are the ones on which ERs are set up in 2 m and 1 m. However, in some cases, these distances can be greater or smaller. These probes are sufficient both for studying rocks along an entire borehole and for detailing individual intervals within a borehole. In the latter case, the ERs are moved from the previous deposits by the appropriate distance (the spacing of the probe).

There are no special multi-conductor cables available at present for logging observations using the CHIM method. KTSH or KTO cable can be braided and thus used instead. Joining three cables into a braid is more or less acceptable. Such a combined cable allows us to use 9 ERs. The element-receivers are connected to the outlets of the corresponding strands of the probes and are fixed to the cable of the probe with the aid of adhesive tape or other similar material.

After filling the element-receivers with the acidic solution, a probe with an ER connected to it is lowered into the borehole. When joining the probe with the cable and the latter with the CHIM-10 station, it is necessary to give special attention to marking the strands and checking for an exact correspondence between the actual connections and the connections recorded in the journal.

Since the length of the probe is always less than the length of the borehole and since logging measurements are carried out for many lowerings and raisings of the ERs, the CHIM measurements in the borehole should be conducted from the top downward in order to exclude errors that might be caused by mixing of the drilling solution during the movement of the cable.

3.1.6. For observations in the aureole and logging versions, we usually use one common auxillary grounding electrode, which is placed no closer than 100 m from the profile or borehole.* One can use iron or steel studs, drive pipe or other similar material as grounding electrodes. It is advisable to place the grounding electrode at a moist site in order to ensure minimal resistance associated with its grounding.

When circular aureole set-ups are used, the auxillary grounding electrodes are best made from iron or steel studs which are arranged in a circle of 0.5-1 m radius around an element-receiver in the center. Usually, 8-10 studs are arranged

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* The distance between the auxillary electrode and the length of the ER line has no effect upon the structure of the field around each ER, since the latter is specially regulated during the selection of the electrochemical extraction regime.

in each circle. All of the studs are joined to a common lead which is connected at its end to a cable which, in turn, is connected to the power supply of the CHIM-10 station.

## 3.2. Selection of Electrochemical Extraction Regimes and Performance of Field Observations

3.2.1. The electrical parameters controlling the electrochemical extraction of elements in the aureole version are the electric field intensity around the element-receiver and the electric current passing through the element-receiver. Each of these parameters is ambiguous in its characterization of the extraction process and varies in the course of the extraction process. The greater the field intensity, the higher the rate of removal of components present in the rock in the water-soluble, mobile state and the more energetic the electrochemical dissolution of the solid phases. Under a constant resistivity of the medium, the current strength increases simultaneously with an increase in the field intensity. Moreover, since the contribution to the total current due to the movements of trace elements of interest (copper, lead, nickel, zinc, etc.) is insignificant, and since the solid phases, which do not contain commercially valuable components dissolve first, the use of higher currents in itself does not mean an increase in the intensity of extraction of the desired elements.

On the one hand, it follows from what has been said above that the electrochemical extraction processes are very complex and antagonistic, and, on the other hand, it follows that the field intensity is the most stable characteristic of this process.

The particulars of electrochemical extraction of elements depending upon the field intensity have not yet been studied sufficiently. Thus, one cannot predict in advance which field intensity will be needed to provide the most effective electrochemical extraction of water-soluble forms of the studied elements within each individual area. However, it has been established experimentally that the required field intensities and extraction times remain constant for different sites within the same region when exploring for mineralizations of the same type. When exploring for ores of a given type within a specific region, it follows that values for the field intensity and extraction time can and should be established experimentally using the appropriate observational regimes at sites with known ore deposits. The selected field intensity and extraction time parameters are assumed to be the baseline data for the study of new areas. When necessary, corrections are made according to the results of the experiments.

3.2.2. The experimental and orientation studies used in selecting a field intensity and extraction time for the given region and type of ore deposit are conducted in the following fashion. Two-three sites with typical for a given region ores are selected and investigations are conducted along two-three profiles within these sites. The profiles are laid out transverse to the strike of the ore zones (bodies). On each profile, extraction of metals is carried out for various (4-5) values of the electric-field intensity: from low values at which the currents through the ERs amount to a few milliamperes to tens of milliamperes, up to the maximal possible values of voltage technically feasible from the CHIM-10 station (current through the ER in hundreds of milliamperes). Intervals of current are designated in steps of 50-100 mA; for example: 50, 100, 200, 300 mA and higher. For hodographs, electrochemical extraction (40-60 hr) is carried out in intervals of 10-20 hr between tests.

Depending upon the specific features of the electrochemical extraction, the hodograph (time vs. accumulation curve) may be straight-line or curvilinear with flattening-out or with an increase in curvature. Flattening-out of the hodograph indicates a preferential intensification of the extraction of accompanying elements in comparison with those of interest. An increase in the curvature of the hodograph serves as an indicator of an intensification of the extraction of the desired elements over the course of time. In general, intensification and weakening with respect to extraction of elements make understanding of the processes difficult and complicate the interpretation of results of observations using the CHIM method. Therefore, a time interval corresponding to straight-line hodographs on all of the points of the profiles should be selected from the hodographs obtained. However, if the observations performed reveal a pattern in which the hodographs flatten out for background points but increase in curvature for anomalous points, it would be favorable to have an extraction time allowing departure of the hodographs to a steadily flattening asymptote for background points and, for anomalous points, a departure to regions of the hodograph with high extraction of masses of desired elements compared with the initial section of the hodograph. The above behavior of the hodographs is related to the presence of well dissolved forms of trace elements above the mineralization and the absence of such forms at a distance from the ores. Such a relationship between types of hodographs serves as a natural contrast intensifier for CHIM-detected anomalies.

When the behavior of the hodographs is complex, a time interval should be selected within the first straight-line portion of the hodographs.*

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** A change in the character of the hodographs is possible in the general case due to additional physico-chemical effects, including specific effects of the electrical current. The phenomena mentioned are still poorly investigated.

Curves of mass (m ) or rate of extraction ($\Delta m/\Delta t$ ) of the metals for the selected time intervals and for each point are designed as a function of the electric field intensity (m - E). For background points, a value of the electric field intensity (E) is selected on an area of the curve characterizing a linear extraction of metals. The value of E should provide an extraction of a mass of metals exceeding the measurement error by a factor of 3-5. Average values for intensity ($E_r$) are calculated for groups of points characterized by similar values of resistivity of the medium. These values are accepted as standards for measurements along the profiles. Subsequently during such measurements, a field intensity is programmed taking into account the values obtained for $E_r$. For identical soil resistivities, the same field intensity is given for all of the ERs. In the case where there are different values of $S_k$ along the profile, the intensity is specified differentially according to reference curves of m-$E_r$ for the corresponding resistivity of the medium.*

3.2.3. An electrochemical extraction regime established for the area (with respect to time and field intensity) and for the types of ores is specified for measurements along profiles in new areas. The extraction regime is established in the following fashion: after connecting up the station and observing measures necessary to ensure a correspondence of connections between the braids and their records in the journal, the entire current is switched on. All of the ERs are switched on in succession at voltages of 25-35 V, the currents are checked in the circuit of each ER and malfunctions are corrected if current is absent. Further measurements of field intensity are made around each ER. Two titanium electrodes are set up at intervals of 20-30 cm on a radius around the ER, and the field intensity ($E_1$, V/m) is measured with the aid of a high-resistance voltmeter. Measurements are made in two mutually perpendicular directions. If the spread of values is greater than 30%, additional measurements are made in two more directions and an average value for $E_1$ is arrived at. Currents ( $\mathcal{I}_1$, A) are recorded individually and the resistivity $S_k$ is calculated.

$$S_k = 0,38 \frac{E_1}{\mathcal{I}_1} , \qquad (4)$$

where 0.38 is the system coefficient for the remote auxiliary grounding electrode.

Furthermore, the currents in each ER are varied in accordance with the field intensity required for electrochemical

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* The problem of selecting the electrochemical extraction regime for rocks with differing resistivities is insufficiently studied and requires further investigation.

extraction of elements and the necessary Er established. The current in this case is determined according to the relationship:

$$I_r = \frac{E_r}{E_1} I_1 \qquad (5)$$

The adjustment period should be brief, no more than an hour for extraction cycles of 10-20 hr.

3.2.4. In contrast to observations in the aureole version, the primary normalizing parameter of electrochemical extraction for logging measurements is the current density or current strength passing through the ER and the ore at its constant with the drilling mud solution. Since the current strength determines the masses of the dissolved minerals and elements arriving at the ER, it is necessary to log the borehole using the CHIM method under identical conditions (dimensions and shape of the ER, composition of the solution within the ER, etc.) and also with identical current density at the borehole walls.

The logging measurements have two purposes: a)identification of ore intervals without outside analytical assaying of the ore grade, and b) quantitative determination of the concentrations of elements of interest within these ore intervals by the CHIM lab.

In the first case, the measurements are carried out under the constant voltage from current source needed to reach the necessary current density in the ore interval facilitating electrochemical solution of the ore minerals.* The current through the ER will vary depending upon the geoelectrical section along the borehole. It will be maximal when crossing ore intervals of lower resistance and minimal when passing "ore-free" intervals of higher resistance. Such a distribution of currents increases the extraction of ore elements from ore intervals relative to extraction from the host rock and allows contrast identification of ores along the borehole. Ores with high resistances that are equal to or less than the resistance of the host rock will be identified satisfactorily, although not as confidently as the ores with low resistances. In zones of brecciation, graphitic rocks, and other areas of lower resistance, however, an increase in current could cause an increased extraction of elements than would be normally expected on the basis of the content of such elements in the host rock. Evaluation of the nature of such intervals requires special attention so that such low-resistance barren zones can be differentiated from the ores.

As mentioned above, it is necessary to normalize the extraction with respect to the current in order to obtain a

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* See "Regime selection" below.

quantitative characterization of the content of elements in the ores. Two conditions must be fulfilled for a correct selection of current density:

a) conditions must be such that the current and extraction time ensure recording of the elements extracted from the ores themselves (and not extracted from the drilling mud solution), that is to say, the conditions match those which occur during the recording of the second branch of the hodograph and when the mass of elements being extracted far exceeds the mass being extracted from the drilling mud.

b) conditions must be such that the selected currents are sufficient for the electrochemical extraction of elements both from massive ores and from veins and disseminated ore.

In principle, the two conditions mentioned could be determined on the basis of calculations. At present, however, the extraction theory is far from being completely worked out, and it is more expedient and reliable to establish experimentall the needed current and time regimes. For the electro-chemical solution of sulfide minerals and components of polymetallic, copper-nickel, and base-metal ores, it has been found experimentally that the following regime is satisfactory: current density at the borehole wall: 7+10 mA/cm$^2$; extraction time: 2 hrs.

However, the indicated extraction regime should be refined in each actual area for the specific type of ore and geoelectrical section. Ore intervals with various structures are selected for this purpose in the area under study. In order to evaluate the extraction regime, one should select ores of all the basic textural types: massive, vein-disseminated and coarsely disseminated zones. Each textural type, together with the geoelectrical characterization, would have clearl features determined on the basis of standard logging methods. It is precisely the characterization of the textural types of mineralized intervals according which will become definitive in the future for the selection of the intensity of current for the electro-chemical extraction of elements, and then for the quantitative determination of the element content.

3.2.5. Observations to determine the dependence of the extracted masses upon the extraction time and current strength are carried out at the selected boreholes. Extraction times of 0.5, 1, 2, and 4 hours are used, along with current densities of 1, 2, 4, 6, 8, 10, and 12 mA/cm$^2$. On the basis of the results obtained, functions of m-j are constructed for various intervals of time. A regime can be considered satisfactory for which the masses of appropriate metals vary linearly with increasing current density. Currents and extraction time are selected so that the mass of each element extracted exceeds the mass of the element during extraction from the drilling solution by a factor of 10 or so that the portion of the element from drilling solution does not exceed 10% of the total extracted mass of the corresponding element.

After the selection of values for the current and extraction time, investigation proceeds on a new borehole. First, the entire borehole is examined in order to identify ore intervals. In this process, the necessary current is selected taking into consideration the ratio between the resistivities of the ore and the host rock. At the first position of the probe in an ore-free portion of the borehole (according to standard logging data), the current used is as many times smaller than the value found during the regime measurements above the ore intervals as the resistivity of the rock is greater than the resistivity of the ores. At the identified ore areas, a detailization is then carried out with a spacing which is specially selected in each individual case. During the detailized observations, the current through each ER is maintained at a constant equal to the current found during the regime observations. The extracted masses are used to charactere the content of elements in the ores (see Section 7).

3.2.6. The extraction of elements is carried out with selected regimes of field intensity and extraction time in the case of the aureole version of the CHIM method, and is carried out with selected regimes of current and time in the logging version.

During the extraction process, the current in the ER is controlled with the aid of a control-measuring instrument set up at the station. The current should be measured regularly at intervals of 2-4 hours for the aureole version and no less frequently than every 0.5 hours for logging observations with a precision of up to a unit of milliampere. The results of the measurements are entered into a journal of observations (see Section 6). Stability of the currents in the ER is an indicator of normal electrochemical extraction. A decrease in the current indicates an increase in the resistance of the grounding of the ER. In the first case, water should be poured on the site of the electrical grounding or the number of grounding electrodes should be increased. In the second case, the contact between the ER and soil should be improved by pouring distilled water under the ER. The total quantity of water poured under the ER should be limited (no more than 0.5 - 1 l). The electric field intensity should be controlled in the area around the ER during the process of electrochemical extraction. During each extraction cycle, the field intensity should be measured no less than once. A fall in current within individual ERs could be connected with an alkalization of the solution. In such a case, acidification of the ER solution should be carried out using concentrated acid. The volume of nitric acid in ml (V ) can be calculated according to the formula:

$$V = 2.7 \cdot I \cdot t,$$

where I is the current in A, t is the time remaining until the end of the extraction cycle, in hours.

The current to the ER is disconnected while adding the acid.

The entire extraction process can be broken up into cycles depending upon the total extraction time. During observations in the aureole version, the usual cycles are 10 and 20 hours. When the total extraction time exceeds the time for a cycle, sampling is carried out between cycles. Sampling is also done after the cessation of the entire extraction process.

3.2.7. The station is disconnected prior to the beginning of sampling. A sign reading "DO NOT SWITCH ON!" "PEOPLE AT WORK!" is hung out on the converter.

The sampling consists in the removal of samples of solutions and the electrodes from the element-receivers. The entire sampling operation requires cleanliness, thoroughness, and accuracy. The test tubes used to take samples are numbered in correspondence to the number on the element-receiver. If the test tubes are covered with polyethylene caps, the address of the ER can be conveniently written on a piece of tracing paper which is sandwiched between two sheets of plastic wrap of the right size; all of this is bound to the butt-end of the test tube with a rubber band. The label should indicate: area, project profile, ER number, sample number, date.

For example:

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Irtysh project
$2_1$
PR 17, 15.06.76

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The test tubes can be covered and fitted with glass stoppers. In this case, the tubes themselves should be numbered. In cases when prolonged preservation of the samples is necessary, a label should be copied and fixed to the side of the test tube.

Test tubes prepared for sampling are placed in a special box with compartments. A half-liter container filled with a solution of acid (the same concentration which is used to fill the ER) is placed in the same box. The pipettes or special syringes which remove samples of the solution from the element-receivers are washed with this acid. The syringe is washed prior to beginning a sample removal from each element-receiver. Acidic solution is drawn in the syringe and drained out into the container for this purpose. The electrodes can be changed during each sampling or only during the last one. After the first sampling is performed, a fresh solution of acid is poured into the element-receiver if extraction has not been completed, and the entire operation: the switching on of the station, the adjustment to the operating regime, the maintaining of a given field intensity and pH, is repeated.

The samples removed are subjected to chemical or physicochemical analysis for elements of interest (see Section 4).

### 3.3. Interfering factors and ways to eliminate them.

3.3.1. Interfering factors include technical malfunctions of the equipment, which can be eliminated in accordance with section 2.5 and in accordance with the maintenance instructions for the CHIM-10 station. Other hindering factors are related to errors in the technological process of the field operations (cleaning of glassware and other materials; the set up of the ER; the maintenance of the selected regimes of field intensity, current strength, and extraction time; the prevention of overalkalization of the ER, the effect of technical contamination), to mistakes due to errors in the analytic operations, and also to certain natural phenomena (meteorological factors, peculiarities of the electrochemical extraction, etc.).

3.3.2. The ERs used, the glassware, the reagents, and other materials should be appropriately clean for observations employing the CHIM method.

Element-receivers in a disassembled state are washed in technical-grade water using a polyethylene brush. They are then placed in a hot (60-70°C) solution of $HNO_3$ at a 1:1 concentration for 15-30 min. Following this, they are pulled from the acid and repeatedly (no less than 5-10 times) washed with technical-grade water and rinsed 2-3 times with distilled water. The rinsed-out ERs are transported in plastic bags. The syringes used to remove samples are washed in analogous fashion.

The titanium electrodes of the ERs are placed in a solution of nitric acid (1:1) and boiled on a water bath for an hour. They are then washed with technical-grade water and rinsed several times with distilled water.

Test tubes and other glass containers used in the removal of samples of solution are first washed with technical-grade water and then placed for several hours (24 hrs.) in hydrochloric acid with a concentration of 1:1, rinsed 2-3 times with distilled water, and dried in a thermostat or in open air. The test tubes are transported in special boxes with compartments. It is recommended that clean test tubes be plugged with glass stoppers (use of rubber stoppers is not allowed!) or plastic wrap. The plastic is first cut into small rectangles and washed, as are the test tubes.

The cleanness of the washed containers and prepared reagents is checked in the following fashion: a solution of acid (approximately of the same normality as the acid which will be used for carrying out the operations) is poured into a washed and assembled ER. The acid is thus kept for a specific amount of time equal to a cycle of electrochemical extraction (10-20 hours). With the aid of the gear for removing samples (pipette, syringe, etc.), a sample of the electrolyte is removed to one of the test tubes prepared for sampling. This operation is performed with 3-5 ERs. A chemical analysis for the appropriate elements is performed. The concentration of metals in such a sample should be 5- 10 times less than the background value for the corresponding metals. For instance, for the Rudnyi Altai the concentrations of lead and copper should not be more than 1-2 mg per volume of ER greater than the background and not more than 50-100 mg per volume greater in the case of iron. In cases of higher concentrations of these elements, the source of the contamination should be found and eliminated. After this, the distilled water and acid are replaced by new distilled water and acid of the appropriate purity. The element-receivers and test tubes are washed one more time and the operation is repeated again. In cases when there is extraction of large masses of elements, it is necessary to wash the ERs with special care.

3.3.3. The errors caused by placing the ERs in different soil layers, errors in maintaining the selected electrical extraction regimes, and also errors involving alkalization of the element-receivers have been discussed in sufficient detail above and do not require further clarification. It is very evident that only when there is a combination of all the measures facilitating identical, normalized conditions of electrochemical extraction can one count on satisfactory results from investigations using the CHIM method for discovery of covered deposits and ore intervals along boreholes.

3.3.4. Fumes from plants and factories, contaminated water waste, ore-transport roads, etc. can cause industrial contamination leading to spurious anomalies. Industrial contamination can be found by direct observations of discharges of material from contamination sources or according to data of the soil survey conducted from the periphery of the areas of contamination to their centers.

Within contaminated areas, it is inadvisable to use the CHIM method in the aureole version, since there are no reliable ways of countering the contamination. In certain cases, however, observations can be performed by setting the ERs within horizons at depths of 30-50 cm or more.

3.3.5. Errors of chemical analysis are a serious factor affecting the results of observations using the CHIM method. Possible sources of error and also measures to eliminate them are discussed in Section 4.

3.3.6. Meteorological conditions, in particular, changes in soil humidity and air temperature, have a significant effect upon the results of measurements using the CHIM method in the aureole version. It is possible that the intensity of anomalies (i.e. concentrations of trace elements) may increase or decrease depending upon changes in humidity, mainly due to the fact that humidity changes the amount of water-soluble forms of elements in the soil. However, it has been found possible to discover anomalies regardless of meteorological conditions. Nevertheless, the intensities of the anomalies relative to the background may change significantly. The anomaly/background contrast is usually reduced during rainy periods.

Methods for countering the effect of meteorological factors on CHIM anomalies have not yet been developed. In order to take into consideration the factors mentioned, it is advisable to collect meteorological data for areas with known ore deposits. CHIM survey should be conducted in accordance with electrochemical extraction regimes experimentally established for each season.

3.3.7. The ways of selecting extraction regimes discussed in section 3.2 require further improvement and also adjustment according to the experience accumulated at many exploration projects. A systematization and classification of electrochemical extraction regimes should be accomplished for various geochemical provinces, geological structures, and meteorological conditions.

### 3.4. Completion of Field Operations. Control and Evalutation of the Quality of the Observations.

3.4.1. After performing the last sampling, cables laid out along the profile or lowered down the boreholes are removed along with the ERs, and the station is returned to the initial position for transport to the next site. The ERs are removed first and washed of impurities such as soil residue and acid at the site. The wires and cables are then wound on their reels. Next, the chemical glassware and containers with working solutions and reagents are carefully packed. Assemblies, instruments, and station installations are checked, secured at appropriate locations, and covered with protective casings. The station is then moved to a new site in accordance with the plan of operation.

3.4.2. The criteria for evaluating the quality of the measurements using the CHIM method are:

a) measures described in sections 3.1-3.3 performed and observations recorded in the field journal; results of the chemical analyses of the samples entered into the journal and also into the diary of the CHIM team. The validity of the results is evaluated according to curves of the mass extraction (m) or rates of extraction (dm/dt) for the various elements along the profile and along the boreholes, and according to hodographs for the corresponding ERs, electric current strengths, electric field intensity, and pH. Information on meteorological, geomorphological, and other conditions and their changes during the measurement period is taken into account.

b) Reproduceability of the results of repeated chemical analyses of individual samples (~ 10%).

c) Similarity of primary and control measurements performed by other teams or the present team under the supervision of the manager, a technical supervisor, or a person specially delegated by them. The volume of control measurements should be no less than the following: in research and development projects, 25%; orientation projects, 15%, and production work, 5%. The CHIM method results are considered satisfactory when the control measurements in the aureole and logging versions allow one to confidently identify anomalous zones with an error in the size of the anomaly does not exceed the spacing of the sampling more than three times.

# 4. ANALYSIS OF SOLUTIONS SAMPLES FROM ELEMENT-RECEIVERS

## 4.1. General Information

4.1.1. The determination of the element concentrations in the samples is the key operation concluding the process of electrochemical extraction of metals and other components from the rocks.

The quality of the analysis has an over-all effect upon the results of investigations using the CHIM method. It is necessary to perform the analysis of solution samples immediately following their removal to avoid irreversible changes in the chemical composition of the samples during prolonged preservation (10 days or more) and to obtain timely information reflecting the quality of the work performed at each site.

All elements capable of travelling under the influence of an electrical current and existing in an ionic form in a solution of the acid used are present in the samples to be analyzed. Out of the total number of elements extracted, the only ones targeted for determination are those which fundamentally characterize the ore deposit sought. Other components can interfere with the determination of the elements of interest and their influence should be eliminated during the course of the analysis. In this section, we present methodologies for determining copper, lead, zinc, iron, nickel, cobalt, and gold which we recommend to analyze for exploration of copper, copper-nickel-cobalt, base-metal and gold deposits. In exploration for other types of ore deposits, it is necessary to review a number of well-known methodologies and adopt them taking into account the specifics of samples obtained by the CHIM method.

4.1.2. We consider a photocolorimetric method the most suitable at this time for determining the content of iron, zinc, cobalt and nickel. The polarographic method using FPL-1 equipment is considered the best for copper, lead and gold. The description of the methods of determination of the above elements follows.

## 4.2. Photocolorimetric determination of elements content.

4.2.1. The photometric method of quantitative analysis is based upon the conversion of a certain component to a light-absorbing compound.* In order to determine the inorganic components, one usually uses reactions forming colored complex compounds possessing characteristic absorption bands in the visible, ultraviolet, or infrared regions of the spectrum. The light

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* A. K. Babko and A. T. Pilipenko. Photometric Analysis. General Information and Equipment. "Khimiya," Moscow, 1988.

absorption is usually directly dependent upon the concentration of the light-absorbing complex and the thickness of the solution layer. The light absorption (optical density) is measured on a photoelectrocolorimeter (PEC).

During work with the PEC prior to performing the analyses (using a series of samples of standard solutions), we construct a calibration graph of the dependence of the optical density of the solution (D) upon the concentration of a specific component (C) within it. The same thickness of absorbing layer is used. For this purpose, 7-10 standard solutions with different concentrations of the specified element are prepared. Enough solutions are prepared to cover the entire range of possible variation in the content of the specified element. The standard solutions are taken through all of the stages of the analysis, as it is done with the test solutions. A "null" solution (blank test) containing all of the materials and reagents that the standard solutions contain is used as a reference solution. It is taken through all of the stages of the analysis but it does not contain the specified element. According to the results on the standards, a calibration graph is constructed which should be a straight line (according to the Ber's law) passing through the origin. The calibration graph is checked in all cases when a new series of working solutions is prepared or when electrolamps, photoelements, etc. in the optical system of the instrument are replaced. The graph is checked at 2-3 points. If the deviation from the graph exceeds 20%, it is necessary to perform calibration measurements again.

4.2.2. Determination of Zinc Content. The methodology* used is based upon the formation of a water-soluble complex compound of zinc with sulfarsacene, colored orange-red. The formed complex is stable under pH 8 - 9.8 and ammonium salts not exceeding 600 mg\l. The maximum of light absorption of this complex occurs when the wavelength reaches 500 m.

Elements interfering in the process of zinc determination are copper, manganese, lead and iron. Copper, manganese and iron form colored complexes with sulpharsacene similar to zinc. In order to eliminate interference effects from manganese and lead, they are bound into colorless complexes by ammonium molibdate. The copper complex formed is destroyed by ascorbic acid, which then reduces the copper to the univalent state. Iron, though it does not form complexes with sulfarsacene, does block the color of the zinc complex. In order to eliminate the interference

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* M. A. Yagodnitsyn and V. N. Antonov. "Accelerated photometric determination of copper and zinc in sewage and natural waters," in: The Purification of Sewage and Circulating Waters in Non-ferrous Metallurgy. Metallurgiya, Moscow (1971), pp. 117-119.

effect of iron, we introduce Seignette's salt, which binds the iron in a colorless complex compound and makes it possible to perform a zinc determination in the presence of 300 micrograms of iron in the volume being analyzed.

Considering the measures which are used to eliminate the effect of copper, manganese, lead, and iron, the methodology allows us to determine zinc with a sensitivity of 1 microgram per 100 ml of solution and a relative error of 15%. Ber's Law is operative within the range of zinc concentrations from 0 to 25 micrograms per 100 ml of solution.

## The Course of Analysis.

Aliquot portions of a sample containing no more than 25 micrograms of zinc are removed to 100-ml graduated flasks and diluted with distilled water to 60-70 ml. Eight drops of a 3% solution of ammonium molybdate are added in order to eliminate the effects of lead and manganese, and 5 ml of a 20% solution of potassium-sodium tartrate (Seignette's salt) are added to eliminate the effect of iron. The samples are carefully mixed after the addition of each reagent. If the pH of the solution is less than 6, the solution is neutralized with a 10% solution of caustic soda to pH 6-7 according to universal indicator paper. An alkaline sample is brought up to a pH of 6-7 with a solution of hydrochloric acid (1:1). Then, 1 ml of an ammonium-chloride buffer solution and 2 ml of a 0.5% solution of sulfarsacene in a 0.05 M solution of sodium borate are added to the neutralized solution and mixed. Eight drops of a 5% solution of ascorbic acid* are added in order to eliminate the effect of the copper. The solution is mixed, brought up to 100 ml with distilled water, and mixed again. The optical density is measured on a REC-56 photoelectrocolorimeter (light filter No. 6, thickness of absorbing layer, 5 cm) in 15-20 min.

A blank test taken through the entire course of the analysis is used as a reference solution.

The zinc content in the sample is determined according to the calibration graph.

## Necessary Reagents:

1. Ammonium molybdate $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$, chemical purity or analytical grade, 3% solution. Three grams of ammonium molybdate are dissolved in 100 ml of distilled water.** Keep no

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* If the amount of copper in the sample is 100 times more than the amount of zinc, then 1 ml of ascorbic acid is added.

** Here and in the other methodologies, only distilled water should be used in the preparation of solutions.

longer than 5 days.

2. Potassium-sodium tartrate, 20% solution. 20 g of potassium-sodium tartrate are dissolved in 100 ml of water.

3. Caustic soda, chemical-purity NaOH, 10% solution. 10 g of alkali are dissolved in 100 ml of water.

4. Ammonium-chloride buffer solution. 54 g of ammonium chloride are dissolved in 500 ml of water, 350 ml of 25% ammonia are added and the volume of the solution is brought up to 1 liter with water.

5. Sulfarsacene, 0.05% solution in 0.05 M solution of sodium borate. To prepare the 0.05 M solution of sodium borate, 12.367 g of boric acid are dissolved in a small quantity of water; 100 ml of a 1 N solution of caustic soda are added and and the mixture is brought up to 1 liter with water. We dissolve 0.05 g of sulfarsacene in 100 ml of a 0.05 M solution of sodium borate. This indicator should be used 12 hours after its preparation.

6. Ascorbic acid, 5% solution. We dissolve 5 g of the acid in 100 ml of water. The solution is prepared for one day's use.

7. Standard zinc solution, 1000 micrograms/ml of zinc. We dissolve 0.1 g of metallic zinc in a small quantity of concentrated nitric acid. The solution is boiled down to 1 ml, 50-60 ml of water is added, and the solution is transfered to a 100-ml graduated flask and brought up to the mark with water.

10 micrograms/ml of zinc: 1 ml of a solution containing 1000 micrograms/ml of zinc is diluted to 100 ml with water.

4.2.3. <u>Determination of Iron Content</u>. The methodology* used is based upon the fact that sulfarsacenic acid in an alkaline medium forms an intensely yellow complex compound with iron (III) ions.

In addition to iron, titanium (lightly yellow), uranium (brown), and several platinoid metals form colored compounds in a neutral or weakly alkaline medium. The interferring effect of these metals is eliminated by the addition of a surplus quantity of ammonia.

Aluminum, calcium, magnesium, rare-earth elements, thorium and beryllium form colorless complexes with sulfosalicylic acid and do not interfere with testing. They, however, can bind

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* S. Yu. Fainberg, Analysis of Ores of Non-ferrous Metals, Metallurgizdat, Moscow, 1953, 832 p.

sulfosalicylic acid thus interfering with the formation of the iron complex. In this case, iron hydroxides can precipitate during the neutrolization of solution, and it will be necessary to add more sulfosalicylic acid to dissolve them and neutralize the solution again.

Manganese and cerium are oxidized in an ammonia solution by atmospheric oxygen and the solution takes on a brownish-red color. If these elements are present in small quantities within the solution, their effect can be eliminated by the addition of muriatic hydroxylamine acid (prior to the neutralization of the solution by ammonia) or hydrazine, reagents which reduce the metals to the divalent state.

In order to increase the sensitivity testing for iron, we measured the final volume of the solution and the thickness of the absorbing layer.

When these methods for eliminating the effect of interferring components are taken into account, the methodology discussed allows one to carry out the testing for iron with a sensitivity of 1 microgram per 25 ml of solution and a relative error of 15%. Ber's law is operative within a range of iron concentrations from 0 to 50 micrograms per 25 ml of solution.

## The Course of the Analysis

Aliquot portions of the solution being analyzed are placed in 25-ml graduated flasks, and 2.5 ml of a 25% solution of sulfosalicylic acid are added (5 ml of a 20% solution of hydroxylamine can be added if need be). The solution is mixed and neutralized with a 25% solution of ammonia until the appearance of a stable yellow color in the solution; then, another 5 ml of ammonia are added. If during this process the solution fogs up (iron hydroxides precipitate), more sulfosalicylic acid is added until suspends disappear, then again the ammonia is added. The solution is then mixed and diluted with water to 25 ml. After 20 min, the optical density of the solution is measured on the PEC-56 (No. 4 light filter, thickness of absorbing layer, 2 cm).

The iron content is determined according to the calibration graph. A blank test serves as the reference solution.

### Necessary reagents:

1. Ammonia water, $NH_4OH$, chemical purity.

2. Hydrochloric acid, HCl, chemical purity, d = 1.17.

3. Nitric acid, $HNO_3$, chemical purity, d = 1.4.

4. Sulfosalicylic acid, chemical purity or analytical grade, 25% solution. 25 g of the salt are dissolved in 100 ml of water. The solution is preserved in vials made of dark glass.

5. Muriatic hydroxylamine or hydrazine, 20% solution; 20 g of the salt are dissolved in 100 ml of water.

6. Hydrochloric acid, 0.1 N solution; 8 ml of the acid with d = 1.17 are placed in a 1-liter graduated flask and brought up to the mark with water.

7. A standard iron solution; 0.7002 g of Mor's salt $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ are dissolved in a small quantity of concentrated hydrochloric acid and evaporated in a dish until moist salts remain; 5 ml of aqua regia (a mixture of concentrated HCl : $HNO_3$ = 3 : 1) are evaporated until dry. Then 5 ml of aqua regia are added again and again evaporated until dry. The dry residue is dissolved in a small quantity of a 0.1 N solution of hydrochloric acid; the solution is transferred to a 100-ml graduated flask and brought up to the mark with a 0.1 N solution of hydrochloric acid. One milliliter of this solution contains 1000 micrograms of $Fe^{3+}$. Solutions with lower concentrations of iron are prepared by diluting the starting solution.

4.2.4. Testing for Copper. The extraction method for determining copper* content is based on the formation of a stable colored complex of copper with lead diethyldithiocarbamate (DDC-Pb) in a layer of carbon tetrachloride at a pH of 2-3. Iron, manganese, cobalt, and nickel form similar complexes with DDC-Pb. In order to eliminate the interfering influence of iron and manganese, ammonium citrate and sodium pyrophosphate are used as complexing agents for masking. Cobalt and nickel interfere with the determination of copper with DDC-lead only when their concentrations are above 10 g/l.

A solution of DDC-copper in carbon tetrachloride possesses maximum light absorption at a wave length of 436 nm (No. 4 light filter). The sensitivity of the copper determination is 0.5 micrograms per 10 ml of solution. The relative error of the determination is 10-15%. Ber's law applies with a range of copper concentrations from 0 to 20 micrograms per 10 ml of solution.

### Course of the Analysis.

An aliguot portion of the sample is placed in a 150-ml separatory funnel; 5 ml of ammonium citrate and 5 ml of sodium pyrophosphate are added; the solution is mixed; and the pH of the

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* L. V. Antropova, M. V. Nedrigailova, A. Z. Shuraleva. Determination of Forms of Occurrence of Copper in Rocks (Methodological Recomendations), ONTI VITR, Leningrad, 1970, 28 pp.

solution is adjusted to 2-3 according to universal indicator paper by adding an ammonia solution (1:1) or hydrochloric acid (1:1). Next, the volume of the solution is brought up to 50 ml with water. Then, 10 ml of DDC-Pb in $CCl_4$ are added and the solution is agitated (shaken) for 2 minutes. After the interlayering of the liquids, the organic layer is filtered into test tubes (with ground-glass stoppers) covered with black paper. The optical density is measured on the PEC-56 (No. 4 light filter, blue; thickness of absorbing layer, 1 cm). A solution of DDC-Pb in $CCl_4$ serves as a reference solution. The optical density of the blank test is calculated from the optical density of each sample analyzed. The copper concentration in the sample is located on the calibration graph.

Necessary reagents:

1. Hydrochloric acid (HCl), chemical purity, d = 1.17.

2. Ammonia ($NH_4OH$), chemical purity, 25% solution.

3. Ammonia citrate, 50% solution; 50 g of citric acid are dissolved in water and the volume is brought up to 100 ml; it is then alkalized with a 25% solution of ammonia to a pH of 8-9 according to universal indicator paper. The solution is transferred to a separatory funnel; 15-20 ml of a solution of Dithizone in carbon tetrachloride are added. The funnel is shaken vigorously, and a new portion of Dithizone is added. The purification operation is repeated until the layer of Dithizone turns green. The residues of Dithizone are extracted from the aqueous solution of ammonia citrate by shaking with several portions of carbon tetrachloride (until the latter is colorless).

4. Sodium pyrophosphate ($Na_4P_2O_7$), chemical purity, 7% solution. 7 g of the salt are dissolved in 100 ml of warm water.

5. Lead diethyldithiocarbamate (DDC-Pb) dissolved in carbon tetrachloride. Two solutions are prepared:
   a) 0.1 g of lead acetate is dissolved in 70-100 ml of water;
   b) 0.1 g of sodium diethyldithiocarbamate (DDC-Na) is dissolved in 70-100 ml of water.

Then the two solutions are poured into a 500-ml separatory funnel, 250 ml of carbon tetrachloride are added, and the solution is shaken until the entire aqueous layer becomes clear. The organic layer is filtered through a dry filter into a dark bottle; 250 ml of carbon tetrachloride are added and carefully mixed.

6. Dithizone dissolved in carbon tetrachloride. 100 ml of $CCl_4$ are poured over the Dithizone (0.1-0.2 g) and the preparation is stored in a dark bottle for 24 hours. Then the solution is

transferred for purification to a 500-ml separatory funnel; 100 ml of an ammonia solution (1 : 100) are added and the mixture is shaken for 1 minute. In order to prevent oxidation of the Dithizone, 1 ml of a 1% solution of ascorbic acid is added to the separatory funnel. The layer with contaminated $CCl_4$ is removed, 50 ml of pure $CCl_4$ are added to the aqueous layer, and then hydrochloric acid is gradually added until an oxidizing reaction occurs. During this operation, the Dithizone moves into the organic layer again. The purified Dithizone is poured into a dark bottle and is kept in a dark place.

7. The standard copper solution; 0.9820 g of copper sulfate ($CuSO_4$ $5H_2O$) is dissolved in 250 ml of 0.1 N hydrochloric acid. One milliliter of this solution contains 1000 micrograms of copper. Solutions with lower concentrations of copper are prepared by diluting the initial solution.

4.2.5. Testing for Nickel, Copper and Cobalt. The methodology* used is based upon the capacity of the metals to form, in an alkaline medium, stable chelated compounds with sodium diethyldithiocarbamate (DDC-Na), which can be easily extracted to the organic-solvent layer and which possess the characteristic absorption spectra. Copper forms a complex with DDC-Na (as it does with DDC-Pb) tinted yellow in the $CCL_4$ layer and posessing an absorption maximum at a wavelength of 436 nm. Cobalt and nickel form complexes with absorption maxima at wavelengths of 365 and 328 nm respectively.

By measuring the optical density of a solution containing nickel, cobalt, and copper using No. 1 (313 nm), No. 2 (365 nm), and No. 4 (436 nm) light filters and solving a system of equations, one can individually determine the quantity of each of these metals.

The interferring effect of a number of elements (iron, manganese, zinc, lead, bismuth, and others) upon the determination of nickel, cobalt, and copper can be eliminated by the introduction of the complexing agents sodium pyrophosphate and ascorbic acid for iron and manganese and by treating the extracts with hydrochloric acid in order to remove lead, zinc, bismuth, and traces of iron and manganese remaining uncomplexed.

## The Course of the Analysis

In order to simultaneously determine nickel, cobalt, and copper, an aliquot portion of the oxidized solution (no more than 25 ml) is placed in a 100-150-ml separatory funnel. The level

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* Yu. P. Shergina, S. S. Shkorbatov, and A. B. Kamiiskaya, Photocolorimetric Determination of Microquantities of Copper, Nickel, and Cobalt during Geochemical Surveys of Copper-Nickel Sulfide Ores, ONTI VITR, Leningrad, 1961, 20 p .

is brought up to 25 ml with water; 2 drops of phenol-red indicator are added along with 5 ml of a 4% solution of sodium pyrophosphate and 5 ml of a 50% solution of ascorbic acid. The pH is adjucted to 8-8.5 with the aid of ammonia (1 : 1) according to universal indicator paper or until a change in the color of phenol red to a pale rose color. To the cooled solution, 2 ml of a 0.1% solution of DDC-Na, and 10 ml of CCL₄ added. The solution is extracted in a separatory funnel over the course of 3 minutes. The extract ($CCl_4$ layer) is filtered through a dry filter ("yellow, white, or red strip") into a dry colorimetric test tube with a ground-glass stopper and is colorimetrized on a PEC-56 photocolorimeter with a mercury lamp in a cuvette (layer-thickness of 2 cm). The optical density of the extract is determined for the No. 1, 2, and 4 light filters. Pure $CCl_4$ serves as the reference solution. The optical-density parameters of the blank sample are deducted from the optical densities of the sample tested on all three light filters. The contents of nickel, cobalt, and copper are determined by the appropriate calculations. The sensitivity of the determination of nickel, cobalt, and copper is 1 micrograms per 10 ml of CCL4, the error of the analysis is 30-40% for 1-2 micrograms concentrations of each of the elements in an aliquot; the error is up to 20% for concentrations above 2 micrograms.

The concentrations of nickel, cobalt, and copper are calculated in the following fashion.

Since three colored components are present in the solution being analyzed, the optical density at each wavelength reflects the influence of the sum of the quantities of nickel, cobalt, and copper:

$$D_{313} = (C_{Cu} \cdot \varepsilon_{Cu}^{313} + C_{Co} \cdot \varepsilon_{Cu}^{313} + C_{Ni} \cdot \varepsilon_{Ni}^{313}) \cdot 1$$

$$D_{365} = (C_{Cu} \cdot \varepsilon_{Cu}^{365} + C_{Co} \cdot \varepsilon_{Co}^{365} + C_{Ni} \cdot \varepsilon_{Ni}^{365}) \cdot 1 \qquad (7)$$

$$D_{436} = (C_{Cu} \cdot \varepsilon_{Cu}^{436} + C_{Co} \cdot \varepsilon_{Co}^{436} + C_{Ni} \cdot \varepsilon_{Ni}^{436}) \cdot 1,$$

where D is the optical density; C is the concentration of the substance in the solution expressed in moles/liter; l is the path length of the penetrating light within the absorbing medium (length of the cuvette), in cm; and is the molar absorption coefficient.

By solving the system of equations (7) for the desired values of $C_{Ni}$, $C_{Co}$ and $C_{Cu}$, we obtain the system of equations (8):

$$C_{Ni} = \frac{D_{313}(\varepsilon^{365}_{Co}\cdot\varepsilon^{436}_{Cu} - \varepsilon^{436}_{Co}\cdot\varepsilon^{365}_{Cu}) - D_{436}(\varepsilon^{365}_{Co}\cdot\varepsilon^{313}_{Cu} - \varepsilon^{365}_{Cu}\cdot\varepsilon^{313}_{Co}) +}{\varepsilon^{365}_{Ni}(\varepsilon^{436}_{Co}\cdot\varepsilon^{313}_{Cu} - \varepsilon^{436}_{Cu}\cdot\varepsilon^{313}_{Co}) - \varepsilon^{436}_{Ni}(\varepsilon^{365}_{Co}\cdot\varepsilon^{313}_{Cu} - \varepsilon^{365}_{Cu}\cdot\varepsilon^{313}_{Co}) +}$$

$$\frac{+D_{365}(\varepsilon^{436}_{Co}\cdot\varepsilon^{313}_{Cu} - \varepsilon^{313}_{Co}\cdot\varepsilon^{436}_{Cu})}{+\varepsilon^{313}_{Ni}(\varepsilon^{436}_{Cu}\cdot\varepsilon^{365}_{Co} - \varepsilon^{436}_{Co}\cdot\varepsilon^{365}_{Cu})} \cdot \frac{1}{1} \qquad (8)$$

$$C_{Co} = \frac{D_{365}\cdot\varepsilon^{436}_{Cu} - D_{436}\cdot\varepsilon^{365}_{Cu} - C_{Ni}(\varepsilon^{365}_{Ni}\cdot\varepsilon^{436}_{Cu} - \varepsilon^{436}_{Ni}\cdot\varepsilon^{365}_{Cu})}{{}^{365}\ {}^{436} - {}^{436}\ {}^{365}} \cdot \frac{1}{1}$$

$$C_{Cu} = \frac{D_{436} - C_{Co}\cdot\varepsilon^{436}_{Co} - C_{Ni}\cdot\varepsilon^{436}_{Ni}}{\varepsilon^{436}_{Cu}} \cdot \frac{1}{1}$$

In order to obtain the value of C, it is necessary to experimentally determine the value of   according to the formula

$$\varepsilon = \frac{D}{C\ 1}$$

using the measurements of D for the three light filters corresponding to the three series of solutions. The first series includes 5 or more solutions with various concentrations of nickel, the second contains cobalt, and the third contains copper. As a result, 9 values of $\varepsilon$ are obtained:

$\varepsilon^{313}_{Ni}$, $\varepsilon^{436}_{Ni}$, $\varepsilon^{365}_{Ni}$, $\varepsilon^{313}_{Co}$, $\varepsilon^{436}_{Co}$, etc.

Substituting these values into equations in (8), we obtain a system of equations with numerical values for the coefficients in front of $D_{313}$, $D_{436}$, and $D_{365}$. For example, a system of equations (9):

$$C_{Ni} = (4,9\ D_{313} - 0,75\ D_{436} - 5,68\ D_{365})\cdot 2,94$$

$$C_{Co} = (7,18\ D_{365} - 0,67\ D_{436} - 1,44\ D_{313})\cdot 2,95 \qquad (9)$$

$$C_{Cu} = (8,25\ D_{436} - 1,59\ D_{365} - 0,9\ D_{313})\cdot 3,18$$

where 2.94, 2.95, and 3.18 are conversion coefficients from

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* Construction of the nomograms is described in detail in the report by L.V. Antropov, et al.: The determination of Forms of Occurence of Nickel in Rocks (Methodological Recommendations). ONTI VITR, Leningrad, 1973, 39 pp.).

g.moles/l to concentrations in micrograms/10 ml.

Using the system of equations (9), we calculate the values of $C_{Ni}$, $C_{Co}$, and $C_{Cu}$ directly on the basis of the measured values of $D_{313}$, $D_{436}$, and $D_{365}$. First, however, one usually calculates and constructs nomograms* on the basis of equations (9); these help to determine the value of C.

Necessary Reagents:

1. Sodium pyrophosphate , 4% solution; 4 g of sodium pyrophosphate are dissolved in water and the solution is brought up to 100 ml.

2. Citric acid, 50% solution; 50 g of the acid are dissolved in water and the solution is brought up to 100 ml.

3. DDC-Na, 0.1% solution; 0.1 g of DDC-Na are dissolved in water and the solution is brought up to 100 ml.

4. The standard solution of copper; 0.9823 g of $CuSO_4 \cdot 5H_2O$ are dissolved in 250 ml of 0.1 n HCl; 1000 micrograms of copper arecontained in 1 ml of this solution. Standards with smaller copper concentrations (10 or 1 micrograms/ml) are prepared according to need.

5. The standard solution of nickel; 1.012 g of $NiCl_2 \cdot 6H_2O$ are dissolved in 250 ml of 0.1 n. HCl; 1000 micrograms of nickel are present in 1 ml of this solution. Standards with smaller nickel concentrations (10 or 1 micrograms/ml) are prepared according to need.

6. The standard solution of cobalt; 1.012 g of $CoCl_2$ $6H_2O$ are dissolved in 250 ml of 0.1 n. HCl; 1000 micrograms of cobalt are present in 1 ml of this solution. Standards with smaller cobalt concentrations (10 or 1 micrograms/ml) are prepared according to need.

7. Phenol red; 0.1 g of indicator pulverized beforehand in a mortar is dissolved by stirring in 2.8 ml of a 0.1 n. solution NaOH and brought up to 500 ml with water.

### 4.3. Polarographic Determination of the Element Content.

4.3.1. The analysis of solution samples from the element-receivers is performed using the method of film polarography with accumulation (FPA) with the aid of the FPL-1 apparatus (a polarograph for field laboratories) in the following fashion.

A negative potential greater than the potential from the electrochemical reduction of the ions of any of the elements is applied to a solid, chemically inert graphite electrode (measuring electrode) immersed in the electrolyte solution being investigated. In the process, the ions of all the elements with reducing potentials less than that of the potential applied at the electrode will be precipitated on the electrode forming "film." Then, the potential of the measuring electrode is measured linearly toward the positive side. During this period, a process of electrochemical oxidation (dissolution) of the reduced on the electrode elements takes place, and these elements are transferred from the "film" form into the solution in ionic form. The process of electrochemical solution of each of the precipitated elements, as well as their precipitation, proceeds to a specific electrode potential which is characteristic for the given element. If a current is detected passing through the studied solution and through the measuring and auxillary electrodes, then a curve of changing current associated with the solution (a change with a specific maximum) will be recorded at the moment each element dissolves. On the basis of the electrode potential that registered the current maximum, one can decide which element is being dissolved from the "films" and, on the basis of the magnitude of the current, can determine the concentration of this element in the solution.

4.3.2. During the course of the analysis, the following operations are carried out:

-the electrodes are prepared,
-the calibration graph is constructed,
-samples are prepared for analysis,
-a curve is made of currents at the moments of the elements dissolution,
-the concentrations and quantities of elements in the sample are calculated,
-the results of the analysis are checked.

The following electrodes are prepared for operation: auxillary, reference, and measuring (graphite).

The auxillary and reference electrodes are prepared in a batch for 50-70 probes and are checked at least once per shift. They are kept in a saturated solution of potassium chloride and the container is filled with this solution to the level of the opening through which the solution is poured. The operating state of the electrodes is checked by measuring the difference in potential between electrodes (without removing them from the potassium-chloride solution) with the aid of a high-resistance millivoltmeter or pH-meter. If the difference in potential between the electrodes is greater than acceptable, i.e+- 5 mV, then the potential of each electrode is checked relative to a control chlor-silver electrode. An electrode which has a potential differing from the potential of the control electrode by more than ±10 mV is replaced by a new one. The control electrodes are stored together with the working electrodes.

The filled and checked electrodes are set on an electrode pulley-block, washed with distilled water, and their ends are immersed in a solution of potassium chloride until the start of the operations.

The measuring electrode is mechanically cleaned after being kept in the air: the thin layer from its butt-end is carefully scraped with a shaving blade and the layer of polyethylene insulating surface is cut at an angle of 45° to the surface. The cleaned butt-end of the electrode should have dull surface without grooves and visible unevenness. The electrode is then fixed to the electrode block and washed with distilled water.

After the described operations, the electrodes are prepared for work.

The calibration graphs used to determine the concentrations of the elements are constructed in the usual fashion. Several (no less than 5) standard solutions are prepared with various concentrations of the specified element within the anticipated range of its content in the analyzed samples. Each standard solution is carried through the entire course of analysis, as is the ordinary sample, and a curve of the current of solution is made for it with the same regimes of current and time as when analyzing the sample. The calibration graph characterizing the dependence of the maximum solution current upon the concentration of the specific element in the standard solutions should be in the form of a straight line starting at the origin (the spread of points should not exceed 20%).

The following solutions are used as the basis for preparing the standard solutions: nitric acid (2 N) for determination of copper, lead, and zinc, and hydrochloric acid (0.1 N) for the determination of gold.

The preparation of the samples for analysis and the selection of regimes for making current curves of the dissolution of elements constitute the methodology of analysis which is given below for each element individually. The concentrations of specific elements found according to the calibration graphs could be verified by a method of additions in the following fashion:

- the graphite electrode is cleaned after recording the curve of the solution current;
- 0.2-0.3 ml of a standard solution of the element at a concentration that will make the concentration obtained in the new solution exceed the original concentration by a factor of "2", are dropped by pipette in the solution being analyzed;
- the solution prepared is analyzed again for the same regimes of current and time.

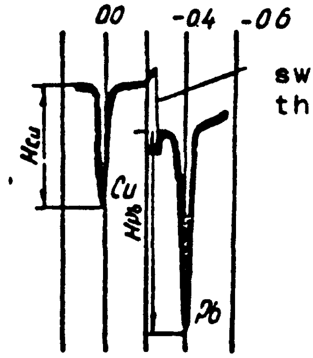
The concentration of the element in the solution being analyzed is determined according to the formula:

$$C_x = \frac{C_{st} \cdot h_x}{H - h_x} \cdot \frac{W_{st}}{V_x} \qquad (10)$$

where $C_x$ and $C_{st}$ are the concentrations of the elements in the analyzed and standard solutions, in micrograms/ml; $h_x$ and H are the heights of the maxima during analysis with and without additions, in mm; $V_x$ and $W_{st}$ are the volumes of the analyzed solution and the added standard solution, in ml. The calculated concentration of the element should not differ by more than 20% from that found according to the calibration graph earlier.

4.3.3. Analysis for Lead and Zinc. An aliquot portion of a solution sample from an element-receiver is evaporated to a volume of about 5 ml in order to remove the nitric oxides, a 0.5 ml solution of $Hg(NO_3)_2$ with a mercury concentration of 1 microgram/ml is added to it, the volume is brought up to 10 ml with water, and the solution is placed in an electrolytic cell which is set on the mounting of the electrode block.
Polarography is carried out under the following conditions: the precipitation potential $\varphi_{prec.} = -0.8$ V; the precipitation time $t_{prec.} = 2$ min; the rate of potential build-up $V_p = 1.2$ V/min; the range of current equals 10 mA for lead and equals 50 mA for copper; the transient period for the solution is 40 sec under "after electrolysis" potential of -0.6 V; the temperature of the solution being analyzed is 20 ±5° C.

The FPL-1 polarograph carries out the operation of precipitation and solution within fixed regimes accompanied by recording of the solution currents on a recording instrument starting automatically when the "cycle" button is pushed.



switching of the current range

Fig. 13. Curves of current indicating the dissolution of lead and copper in nitric acid.

Maximum currents are established for lead at a potential of ~ -0.4 V and for copper at ~ -0.0 V on the basis of the recorded curve of solution points (Fig. 13).

The analysis for lead is possible in the presence of copper, cadmium, antimony, bismuth and iron (III) if the ratio of lead concentration to these elements in the solution being analyzed does not exceed:

Pb : Cu = 1 : 15
Pb : Cd = 1 : 100
Pb : Sb = 1 : 20
Pb : Bi = 1 : 20
Pb : Fe = 1 : 100 (when ascorbic acid is added)

Analysis for copper is possible in the presence of lead, cadmium, and trivalent iron if the ratio of concentration of copper to these elements in the solution being analyzed does not exceed:

Cu : Pb = 1 : 15
Cu : Cd = 1 : 100
Cu : Sb = 10 : 1
Cu : Bi = 10 : 1
Cu : Fe = 1 : 1000 (when ascorbic acid is added)

Necessary Reagents

1. Nitric acid, $HNO_3$, chemical purity, 2 N solution; 14 ml of concentrated acid are diluted to 100 ml with water.

2. Mercury nitrate. $Hg(NO_3)_2$; 1 g of metallic mercury (high purity, grade R-OD, RETU 1252-65) is placed in a Kjeldahl flask and dissolved with heat in 50 ml of a 50% solution of nitric acid.

After dissolving, the completeness of the oxidation of metallic mercury to $Hg^{2+}$ is checked. For this purpose, a drop of the solution is placed on a watch glass and several drops of concentrated hydrochloric acid are added. If a white precipitate of calomel forms, another 50 ml of a 50% solution of nitric acid is added and the mixture is heated again. After complete oxidation of the mercury (the absence of white precipitate), the solution is evaporated to 20-25 ml in order to remove the nitric oxides. The solution is cooled and transferred to a 1-liter graduated flask. The solution is brought up to the mark with a 2 N solution of $HNO_3$. The solution obtained contains 1 mg/ml of $Hg^{2+}$.

3. Standard solutions of lead and copper:

160 mg of $Pb(NO_3)_2$ are dissolved in 100 ml of 2 N $HNO_3$; 1 ml of this solution contains 1000 micrograms of $Pb^{2+}$.

456.5 mg of $Cu(NO_3)_2 \cdot 6H_2O$ are dissolved in 100 ml of 2 N $HNO_3$; 1 ml of this solution contains 1000 micrograms of $Cu^{2+}$.

A solution containing 10 micrograms/ml Cu and Pb is prepared in the following way: 1 ml aliquots of solutions of $Cu(NO_3)_2$ $6H_2O$ and $Pb(NO_3)_2$ containing 1000 micrograms/ml of $Cu^{2+}$ and 1000 micrograms/ml of $Pb^{2+}$ respectively are removed one at a time to a 100-ml graduated flask and brought up to to the mark with water.

4.3.4. Determination of Gold. The solutions from the element-receivers are treated beforehand in order to separate the gold from interferring elements: iron, mercury, the platinoid metals, and also $NO_3^-$. The determination of gold is based upon its extraction in the form of $AuCl_4^-$ in ehtyl acetate.

Samples of solution from an element-receiver are placed in a heat-stabilized 50-ml, 3-5 drops of a 2% solution of NaCl are added, and the mixture is evaporated to a volume of approximately 3-5 ml in order to remove the nitric oxides. The volume is brought up to 20 ml with water and the mixture transferred to a separatory funnel. The mixture is diluted with 5 ml of concentrated hydrochloric acid and 10 ml of ethyl acetate, and left 1 minute for extraction. For a better separation of the aqueous and organic phases, 1 drop of methyl orange is introduced; the aqueous layer is tinted red in the process. After extraction, the phases are separated: the aqueous phase (which is located on the bottom) is poured off and the ethyl acetate is washed twice with 10 ml of 0.1 N hydrochloric acid for 30 sec each time. Washed ethyl acetate is placed in a 50-ml heat-stabilized beaker; 3 drops of a 2% solution of NaCl is added and the mixture is evaporated to dryness. The gold compounds are very volatile, therefore, heating should be at no more than 100°C. The sample is evaporated in a water bath, but an electric plate wrapped in 2-3 layers of asbestos can be used. The temperature of the plate is best regulated so that the water in the heat-stable beaker does not boil.

To the hot, dry residue, 0.5 m of aqua regia and 3 drops of hydrogen peroxide are added; the mixture is evaporated to moist salts. The hot residue of 0.5 ml of hydrochloric acid is then treated twice (in order to remove nitric oxides). The hot, dry residue is flooded with 5 ml of a base electrolyte, a 0.1 N solution of hydrochloric acid.

All of the operations related to the treatment of the sample after evaporation should be performed only in the hot beaker, without allowing the beaker to cool.

When the concentration of electrolyte is increased from 0.1 to 2 N, the peaks caused by gold are decreased by a factor of 2; therefore, it is necessary to carefully maintain the acidity of the base electrolyte. In order to accomplish this, the concentrated hydrochloric acid is completely evaporated after the last treatment, not allowing the precipitate to overincandesce.

Polarography is carried out under the following conditions: the precipitation potential $\varphi_{prec}$ = -0.6 V; the precipitation time $t_{prec}$ = 5 min; the rate of potential build-up $V_p$ = 1.5-1.8 V/min; the range of current equals 2 mA; the transient period of the solution is 40 sec at an "after electrolysis" potential of +0.3 V; the temperature of the solution being analyzed is 20±5°C; the sensitivity of the analysis is 0.01 micrograms/ml, i. e., 0.05 micrograms of gold can be found in 50 ml of a sample from an ER when the sample is concentrated down to 5 ml. The allowed concentrations (micrograms/ml) of extraneous elements reached in the solution being analyzed after extraction are: Ag, Pb, Hg, Bi, Sn, Cd: up to 2; Hg:up to 0.6; Fe: up to 10; As, Sb: up to 1; Cu: up to 0.1 micrograms/ml.

<u>Necessary Reagents</u>

1. Hydrochloric acid, concentrated, chemical purity or purified, d - 1.19.

2. Hydrochloric acid, 0.1 N, 8 ml of hydrochloric acid (d = 1.19) are added to a graduated flask and the solution is brought up to 1 liter with water.

3. Nitric acid ($HNO_3$), concentrated, chemical purity or purified.

4. Sodium chloride (NaCl), 2% solution; 2 g of NaCl, c. p. grade (recrystallized or calcined in a muffle at t° = 500-600°C for 3-5 hours) are dissolved in 100 ml of water.

5. Potassium chloride, KCl, chemical purity.

6. Hydrogen peroxide (perhydride, $H_2O_2$), d = 1.112. Store in bottles of dark glass with ground glass stoppers.

7. The standard gold solution is 1000 micrograms/ml. We dissolve 0.1000 g of gold of an appropriate purity (better if 99.99%) in 4 ml of aqua regia (3 ml of concentrated HCl and 1 ml of concentrated $HNO_3$).

The solution obtained is evaporated almost to dryness; 2 ml of concentrated HCl is added to the residue; and still another 2 ml of concentrated HCl are added after evaporation to moist salts. The mixture is again evaporated to half its volume and the mixture is diluted up to 100 ml with water in a graduated flask. It is recommended that 3 ml of a 2% solution of NaCl be added to 100 ml of the standard in order to stabilize the solutions.

The working standard solutions are prepared by appropriate dilution of the stock solution with a 0.1 N hydrochloric acid.

8. Ethyl acetate (acetate, $CH_3COOC_2H_5$), d = 0.901, chemical purity, EXPLOSIVE AND FLAMMABLE!

9. Aqua regia, a mixture of concentrated acids HCl and $HNO_3$ (3 : 1), is prepared prior to the chemical treatment of the samples.

10. Distilled water. We add 2-3 drops of ammonia to the water obtained from the distiller and filter it through activated charcoal.

4.3.5. Determination of Zinc. For zinc analysis of solution samples from the element-receivers, the measuring graphite electrode is first amalgamated in order to differentiate reduction potentials of zinc ions and hydrogen, resulting from the shift of the potential for hydrogen to the negative side, and also to prevent the formation of intermetallic compounds of zinc with other elements which are reduced on graphite and which interfere with satisfactory subsequent solution of the precipitated zinc. In addition, the sample of solution from the ER is first treated with sodium acetate to exclude the influence of iron.

Precipitation of a film of metallic mercury on the graphite electrode is carried out prior to the analysis of each sample. We place 10 ml of a solution of mercury containing 2 mg/ml $Hg^{2+}$ (2 N with respect to $HNO_3$) in a cell. Electrolysis of the mixing solution is carried out for 1 min at a potential of the graphite electrode equal to - 0.3 V. At this potential, the electrode is then removed from the solution and carefully washed with distilled water.

An aliquot portion of a sample from an ER is placed in a 50-ml heat-stabilized beaker and evaporated to dryness. The precipitate is dissolved in 10 ml of a 0.1 M solution of sodium acetate while being heated in the beaker covered with a watch glass. It is advisable to boil the solution for 1-2 minutes in order to precipitate the iron. If iron precipitates the solution is poured off without the precipitate and is brought up to 10 ml with sodium acetate for polarography. Filtering of the solution is not recommended. In cases when an iron precipitate is absent, the boiled solution is brought up to 10 ml with a 0.1 M solution of sodium acetate.

Polarography is carried under for the following regimes: precipitation potential $\varphi_{prec}$ = - 1.5 V; precipitation time $t_{prec}$ = 1 min; rate of potential build-up Vp = 1.4-1.6 V/min; range of current, 10 mA; transient period of the solution, 40 sec at an "after electrolysis" potential of 1.3 V; temperature of the solution being analyzed, 20+5°C; potential of zinc solution located within the range of -1.0 to -1.2 V; mimimal determined concentration of zinc, 0.1 micrograms/ml. Determination of zinc is possible in the presence of: iron (trivalent), up to 30 micrograms/ml; copper, 0.05 micrograms/ml; lead, 10 micrograms/ml; cadmium, antimony, and tin, 1.0 micrograms/ml; manganese, 10 micrograms/ml.

Necessary Reagents

1. Mercury nitrate $(HgNO_3)_2$. We place 2 g of metallic mercury (high purity, grade R-OD, RETU 1252-65) in a Kjeldahl flask and dissolve it while heating in 50 ml of a 50% solution of nitric acid (c. p.). After dissolving the metallic mercury, a check is made for complete oxidation of the metallic mercury to $Hg^{2+}$. A drop of the solution is placed on a watch glass and concentrated hydrochloric acid is added. If a white precipitation of calomel forms, another 50 ml of 50% nitric acid are added and the mixture is heated again. When the mercury is completely oxidized (the absence of a white precipitate or cloudiness), the solution is evaporated to 20-25 ml in order to remove nitric oxides. The solution is cooled, transferred to a 1-liter graduated flask and brought up to mark with a solution of nitric acid. The solution obtained contains 2000 micrograms/ml of $Hg^{2+}$.

2. Sodium acetate $(CH_3COONa \cdot 3H2O)$,1 M, with concentrated acetic acid. We dissolve 13.6 g of sodium acetate (three waters of hydration, c. p.) in a small quantity of distilled water, add 10 ml of concentrated acetic acid, and bring it up to 1 liter with water.

3. The standard zinc solution. We dissolve 454.7 mg of $Zn(NO_3)_2 \cdot 6H2O$ in 100 ml of 2 N. $HNO_3$; 1 ml of this solution contains 1000 micrograms/ml $Zn^{2+}$.

A solution containing 10 micrograms/ml of $Zn^{2+}$ is prepared by diluting the stock solution one-hundred-fold with water.

# 5. SAFETY PROCEDURES

## 5.1. General Considerations

5.1.1. During field investigations using the CHIM method and when utilizing the CHIM-10 station, it is necessary to abide by: appropriate technical manual and the station maintenance manual, instructions for the maintenance of the self-powered PK-2 logging hoist, the use of the polarograph for the PPL-1 field laboratories, "Unified Safety Rules for Geological Exploration Operations," "Instructions for Carrying Out Geophysical Investigations in Boreholes," "Instructions on Safety Procedures During Laboratory Research," "Safety Rules for Maintenance of Electrical Equipment of Stations and Substations," and "Safety Rules for Technical Maintenance and Safe Operation of Electrical Equipment in Industrial Enterprises."

Only employees who have passed an examination on safety procedures are allowed to work at the CHIM-10 station. The operation personnel of the station should have an electrotechnical qualification rank of not less than II and the team chief should have an electrotechnical qualification rank of not less than III. Review instructions on safety procedure should be presented no less than semiannually. The dates of training sessions and the review inservices on safety should be recorded in a journal for recording training and instructions of employees on safety policies and procedures; this journal should be kept by the CHIM team chief.

Individual and group protection gear should be available at the CHIM-10 station. These include: non-conductive gloves, rubber galoshes, and mats which are periodically checked in accordance with existing norms; acid-resistant aprons and gloves, and neutralizing solution effective against acids and alkalis, etc.

A set of warning and prohibiting signs should be available at the station, and also flexible safety cords with red flags and total lengths long enough to provide safety along the profiles being studied and over the area where the station is positioned. The signs can be fixed on the walls of the truck cabin and the diesel assembly. Some signs are arranged along the safety line with red flags.

Responsibility for safety procedures within the CHIM team rests with the team chief.

5.1.2. After prolonged storage or after being in a non-operating state for longer than a month, the insulation resistance of current-bearing power circuits in the loops of the apparatus should be checked before switching it on, along with the operational state of the blocking system of the station. The station is generally checked at least semiannually in the process of its exploitation.

The insulation resistance of the power circuits can be checked when the equipment is disconnected using a M1101M-type 500 or 1000 V megohmmeter. When the insulation resistance is below 500 kohm, the damage should be found and eliminated.

The blocking system should be checked for load resistance with apparatus working and power circuits connected . At the moment the gate is opened or the units protected by blockers are opened, the contactor in the protection unit should actuate and the entire station should shut down.

The results of the check of the resistance of the power circuits insulation, and also the efficiency check of the blocking systems are recorded in the form of a statement of the station's technical condition. This statement is signed by the project chief or a person responsible for safe conduct of the operations, by the chief of the CHIM team, and by a representative of the trade-union organization. The statement also addresses the completeness of the station's inventory of individual and group safety equipment and the adequacy of the warning signs, and confirms that the protective unit in the AD-10 assembly is sealed.

## 5.2. Safety Measures When Carrying Out Operations

5.2.1. Prior to the Start of Operations. The CHIM-10 station is positioned at the field-work site in a way that provides a visual link between persons operating the station and the AD-10 assembly, and that makes it possible to view a major portion of the profile from the station during observations in the aureole version or makes it possible to view the borehole opening and the hoist during logging measurements.

The equipment of the station is connected to a protective grounding with a contact resistance which should not exceed 10 ohm.

The positioning of the station and the AD-10 trailer should exclude the possibility of a spread of exhaust gases from the diesel-electric assembly to the station and a spread of gases released from the chemical laboratory to the diesel-electric assembly.

When roads and other communications are transversed by profiles, cables should be suspended or dug in, and warning signs stating "Attention! Cable!" should be posted.

For logging observations, the following should be checked prior to the start of the hoisting operation: the hoist brake, the secure fixation of the block balance, the presence of casings for rotating mechanical assemblies, and stabilizing base blocks.

5.2.2. During the Observational Process. The mechanisms and assemblies that comprise the CHIM-10 station are turned on during operation or turned off only upon the command of the team chief or, in accordance with a schedule in the logs, upon the command of the senior technician (operator) on duty. Prior to transmitting voltage to the line, the operator should make sure that others are not near the station and should give a warning signal.

Two workers wearing slip-on, non-conducting gloves and galoshes measure the field intensity during the time the station is operating. Work on the element-receivers (addition of acids, checks of contacts, etc.) is only allowed after disconnecting the current in the corresponding line of the element-receiver. Supplying voltage to an element-receiver raised out of the borehole is forbidden. The diesel-electric assembly should be serviced only by persons qualified to service power equipment. Containers with combustible materials should be set up no closer than 5 m from the AD-10 at a site protected from falling sparks.

First aid kit and fire extinguishing equipment should be located in an accessible place and should be ready for immediate use.

At night, the the station camp and the cable lines should be lit with lights attached to the roof of the station truck bed. When there is no direct visibility, additional lights should be set up at appropriate locations along the profile.

5.2.3. Working with Chemical Reagents on the Profile (Borehole). Persons who have completed special instruction are qualified to work with the chemical reagents. The reagents should be stored in tightly covered containers with the names of the reagents clearly written out. It is necessary that the reagents only be transported in special packing to protect them from damage.

Preparing of the necessary solutions of chemical reagents at the required concentrations and also pouring of the reagents into the ER should only be done wearing rubber gloves and protective goggles.

During the station operations, large volumes of chemical reagents (bottles, canisters, etc.) are stored outdoors at a specially marked-off site protected from sun and atmospheric precipitation.

Prior to pouring acid into a logging element-receiver and removing samples from it, the cable from the ER should be secured on a special pole.

5.2.4. Work in the Chemical Laboratory. Persons not connected with performing the analyses are forbidden entry to the chemical laboratory.

The chemical reagents should be stored in special packing at sites marked off for them. When performing analyses, the appropriate chemical reagents should be kept in the exhaust cabinet. The exhaust ventillator should draw off air at a rate of no less than 1 m/sec.

Use of electric plates and other electrical equipment with damaged insulation on current-bearing parts is forbidden. The reagents should be located at a great enough distance from the plates to prevent them from being heated. Evaporation of solutions should only be done in the exhaust cabinet with the protective glass shut.

## 6. DOCUMENTATION, QUALITY CONTROL AND ACCOUNTABILITY

6.1. The primary documents for measurements using the method of partial extraction of metals are the following:

a) a journal of field observations,
b) a journal of results of chemical analyses,
c) graphs of the extraction of metals along the profiles (for the aureole version) and in the boreholes (for logging version).

6.2. The journal of field observations is maintained by the team chief and the technician on duty. The team, the area of operations, persons responsible for carrying out the measurements and keeping the records, the address of the home office of the organization,' and the dates of initiation and completion of the work should be shown on the title page of the journal.

For work in the aureole version, the geologic and geomorphologic features in the area of operation and the soil types are briefly described on the first page of the journal. The horizon in the soil profile at which the ERs are set up is also indicated on this page, and a small sketch along the profile at a scale of 1 : 1000-1 : 2000 is pasted in. On the next page of the journal (Fig. 14), data from all of the measurements associated with setting up the extraction regime, the current in the ER (in mA), the switching-on and switching-off times for the station, and the results of chemical analyses of the sample after the completion of the extraction cycle are presented in sequence.

For logging observations, the journal is filled in according to the graphs presented (Fig. 15). The interval between ER set-ups, the extraction time, the current in each ER, the total voltage and the total current are recorded.

6.3. A journal of the results of the chemical analyses is maintained by the team's chemist. The title page is filled in the same manner as the journal of field observations. The next pages are filled in according to the graphs shown in the journal (Fig. 16). The current and height of peak are described in graphs 7 and 8 for work with FPL-1, and the optical density of the solution is noted for work with the PEC.

6.4. Curves for the extraction of the metals are constructed by the team chief immediately after the results of the chemical analyses are obtained. For clarity, it is recommended that curves for the extraction of individual metals be represented on a single graph by the use of differently colored lines, for instance, with solid lines: lead - red, nickel - violet, gold - yellow, zinc - blue, tin - brown, copper - orange, iron - black; with dotted line: arsenic - green, cobalt - blue.

The vertical scale on the graphs is selected in such a way that the background values for extracted quantities of metals do not exceed 5 mm. The horizontal scale is determined by the scale of the survey. On the graphs, areas with anomalous values are delineated with horizontal hatchuring down to the background level.

The background level can be estimated visually: it is characterized by a predominance of low and similar to each other quantities of extracted metals in barren areas. Individual samples or groups of samples with higher quantities of extracted elements can be distinguished against the background level.

A more precise estimate of background ($M_b$) and anomalous ($M_a$) masses of extracted elements can be achieved by processing the analyses 'data using statistical methods. The masses $M_b$ and $M_a$ can be determined by either graphic method or calculations.

In order to evaluate the reliability of the measurement results, graphs of repeated observations are constructed: along profiles (for the aureole version) and downhole profiles (for logging version). Anomalous zones on repeated graphs should spatially coincide. Margin of error should not exceed three times the spacing along the profile. For logging measurements, the margin of error should not exceed three times the interval between points of observation downhole.

6.5. In addition to the enumerated primary documents, the CHIM team should also have the following:

a) assignments and calendar of operations;

b) geological and geophysical data on the region being studied (for the aureole version) and borehole logging data (for the logging version);

c) a team diary;

d) a journal for reports of changing work shifts;

e) a journal accounting for the work time of diesel-electric station ESD-10;

f) a journal of instruction on safety procedures.

6.6. Exploration justifications for using the CHIM method along with the project objectives, the amount of work and the deadlines involved are indicated in the assignment to the CHIM team. The team chief selects the appropriate sites on the basis of this information. The team chief also compiles a calendar of operations which should be agreed upon by the persons responsible for the drilling and geophysical operations at the given sites and which should be authorized by senior management (the Chief Project Engineer or regional authorities). The graphs are compiled in such a way that the geological information obtained on the basis of the CHIM results can be opportunely used for positioning of future drillholes or redrilling of ore intervals.

6.7. Included in the geological and geophysical materials on the site being studied, are extracts and print-outs necessary for the interpretation of surface observations using the CHIM method in the aureole version, data on standard borehole logging, geological sections (downhole), geological columns, and the results of chemical or spectral analyses of core during operation in the logging version.

6.8. The nature of the operations carried out during the day, their organization, the condition of the technical and transportation gear, and the liabilities of the team co-workers are indicated in the diary. The diary entries are made by the team chief on a daily basis.

6.9. Journals of procedures and on the surrendering of work shifts, and instructions on safety procedures are kept in generally accepted formats in accordance with the rules for safety procedures and the daily schedules.

6.10. In the journal accounting for the operating time of the diesel-electric ESD-10, the total time of the assembly's operation is noted along with the time required to service it in accordance with the manual.

6.11. One-two days after the completion of operations at the site (in the aureole version) or at the borehole (in the logging version), the team chief draws up a written summary. The goals and objectives of the investigations, the methodology for solving problems that takes into account specific characteristics of the work site, the results of interpretations of graphs for the extraction of metals along the profile (profiles) or borehole are noted in the conclusion.

The following are presented in the graphic appendix to the summary: for the aureole version -- curves for the extraction of metals along profiles drawn on a geological map to which data from geophysical observations have been transferred; for the logging version -- diagrams of logging observations using the CHIM method and standard logging.

Reports that consist of the written summary and graphs of observations using the CHIM method are made in two copies: one remains with the CHIM team and the other to be sent to the Project Manager.

6.12. All of the enumerated primary, secondary, and summary documents (sections 6.1-6.3) are presented to the quality control commission. The quality of field information is determined according to the requirements of Section 3.

On the basis of the compiled documents, the team chief writes final reports (enclosing the necessary graphs, cumulative tables, etc. in accordance with the accepted system of documentation for field projects).

## 7. DEFINING THE LOCATION AND COMPOSITION OF MINERALIZATION

7.1. The CHIM method allows identification of ore mineralization on the basis of high (anomalous) values for extracted metals. The logging version provides a direct determination of the composition and location of ore intervals on the drillhole by direct recording of metals content extracted electrochemically from the ores. The aureole version makes it possible to infer indirectry the location of ore mineralization beneath cover using the contents of trace elements and outline the position of their secondary dispersion aureole. Accordingly, the reliability of these two approaches will be different.

7.2. To interpret the CHIM data in the aureole version, we use the same approach as for grid soil geochemical survey based on secondary dispersion aureoles. In it, zones of mineralization and potential ore deposits are contoured in plan view according to anomalous, amounts of trace elements. The type of potential mineralization is determined according to anomalous trace elements. The CHIM results in the form of graphs or contour lines of the masses of extracted metals allows one to do the same (Fig. 17).

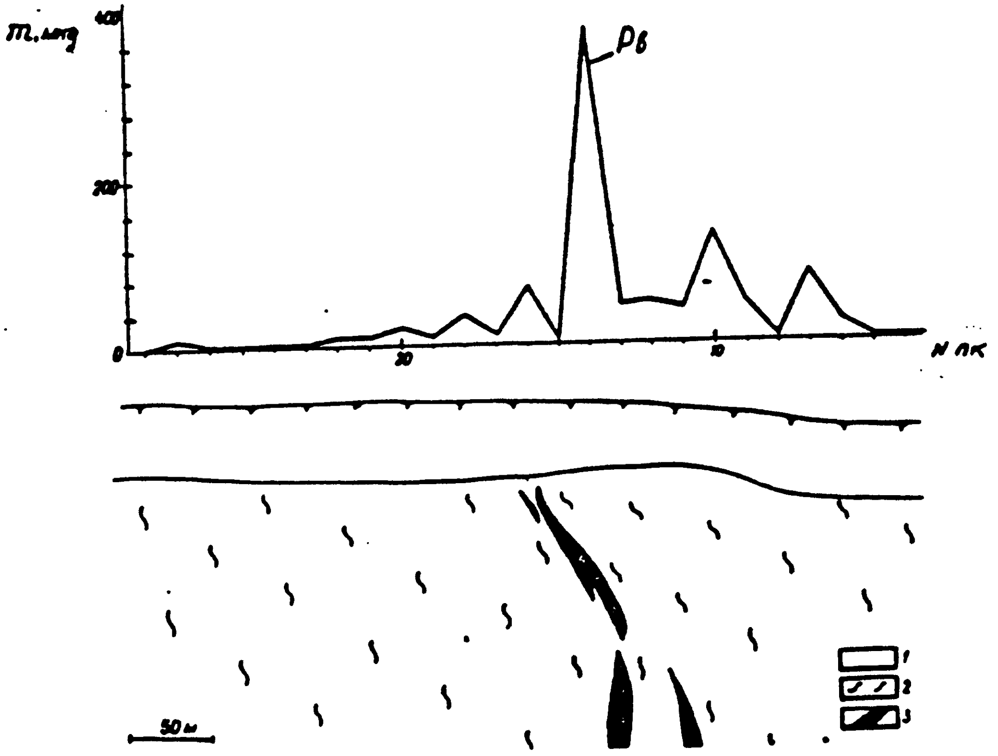


Fig. 17. The CHIM method results in the aureole version:
1) unconsolidated sediments, 2) volcanic and sedimentary rocks, 3) polymetallic mineralization.

The CHIM method in the aureole version is the most reliable for tracing ore bodies on the flanks of known deposits in areas covered with unconsolidated sediments and inaccessible to other geophysical and geochemical methods. It can also be used with confidence to characterize the chemical compositions of ore detected by geophysical methods (induced polarization, charge, and others), on the basis of elements extraction in anomalous areas. In this case, the identification and separation from each other by CHIM method of carbonaceous-graphitic rocks, pyritized and pyrrhotite-bearing zones, and polymetallic and copper-nickel deposits is of special significance. Carbonaceous-graphitic rocks are not accompanied by CHIM anomalies involving any types of metals. Only the increased extraction of iron and an absence of significant extraction of lead, copper, zinc, nickel, and other ore components are characteristic of pyritized and pyrrhotized zones. Anomalies of those metals which constitute the ore will be detected above the deposits.

The results of the CHIM method might be quite uncertain as far as the scope of potential mineralization in the newly discovered anomalous area is concerned. The CHIM data may serve as a basis for further exploration efforts designed to give a quantitative test to mineralization.

7.3. The CHIM results in logging allow one to determine the location and composition of ore bodies.

It is possible to establish the elements content and the location of the ore interval downhole. The accuracy of the determination of the ore-interval boundary depends upon the spacing of the element-receivers and also upon several technical conditions associated with the measurements. In particular, it is possible to underestimate the depth of the ore interval because of the downmovement of the metal-extracting solution (which can be denser than the circulating fluid) toward the bottom of the borehole. A detailization is carried out for increased accuracy in determining the boundaries of the mineralization within the area. The usual error in determining the position of the ore body equals half the spacing for the array of element-receivers. However, technical and other factors can lead to an increase in error. Experience at conducting observations shows that often the error does not exceed three times the spacing of the element-receiver array. When the detailization step is 10-25 cm, the error in determining the boundaries and the position of the mineralization often turns out to be within a few tens of centimeters.

The element content can be calculated according to the formula:

$$C_i = P_{i,T} \cdot m_i \qquad \text{(II)}$$

The magnitude of $P_{i,T}$, as shown in sections 1 and 3, can be established for a studied region experimentally for each element (i) and each texture type of ore (T).

The ore texture is established in standard logging: for electroconductive ores, according to MSK and MEP geophysical survey data; for nonconductive ores distinguishable by density and magnetic properties, according to the results of a density log (gamma-log) and a log of magnetic susceptibility.

If, for example, $l$ is an electroconductive ore interval and $\Sigma_\Delta l$ is the sum of lengths of electroconductive regions within this interval along the axis downhole, then $\gamma = \frac{\Sigma_\Delta l}{l} \cdot 100$ characterizes the texture and bonding of electroconductive minerals in the mineralization. The texture of the ore can then be characterized for $80 < \gamma < 100$ as solid; for $50 < \gamma < 80$ as veinous; .for $50 < \gamma < 20$ as veinous-disseminated; and for $\gamma < 20$ as disseminated. These gradations in texture will have their own P values for each metal. In the general case, $P = f(\gamma)$, and the error C can be estimated to within tens of percentage points. It is possible to determine P more accurately if one uses $\beta = \frac{\Sigma_\Delta S}{S} \cdot 100$ instead, where S and $\Delta S$ are the areas of the ore-interval surface and the electroconductive regions. They can be determined on the basis of logging data (MSK or MEP) from a few boreholes in progress.

Values of $P_{i,T}$ for each metal and textural type of ore are established according to results of measurements of known ore intervals for an electric extraction regime selected in accordance with Section 3.2.5. The value of $P_{i,T}$ is determined according to formula (II). Values of $C_i$ are known as a result of chemical analysis of the core from the boreholes, and $m_i$ is determined on the basis of sampling of the ERs. Since the $m_i$ depends on the electric current and the time of leahing, the corresponding values of $P_{i,T}$ are related to their associated values of $I_i$ and $t_i$. Since the extraction regimes selected should apply to conditions involving a direct proportionality of the masses extracted upon the current and extraction time, it is expedient to relate $m_i$ to $I_i$ and $t_i$ using the quantity $m_i/I_i t_i$. Accordingly, the values of $P_{i,T}$ should also be related to $I_i$ and $t_i$ or $P_{i,T} = P'_{i,T}/I_i t_i$, where $P'_{i,T}$ corresponds to the value of $m_i$, and $P_{i,T} = m_i/I_i t_i$.

The contents of known elements in newly discovered ore intervals are determined according to the values found for $P_{i,T}$. The results of the determination are recorded in the form of a table (see TABLE 1) positioned alongside curves for the extraction of the metals (Fig. 18).

TABLE 1.

| Ore Types | Interval downhole, in m | Elements content (%) based on data of | | | |
|---|---|---|---|---|---|
| | | Chemical analysis | | CHIM method | |
| | | Pb | Cu | Pb | Cu |
| Vein-disseminated | 217,1-220,5 | 0,86 | 2,44 | 0,45 | 2,30 |
| Disseminated | 259,0-261,0 | 0,05 | 0,12 | | |
| | 261,0-262,0 | 0,05 | 1,88 | 0,03 | 0,44 |
| | 262,0-263,0 | 0,13 | 0,56 | | |

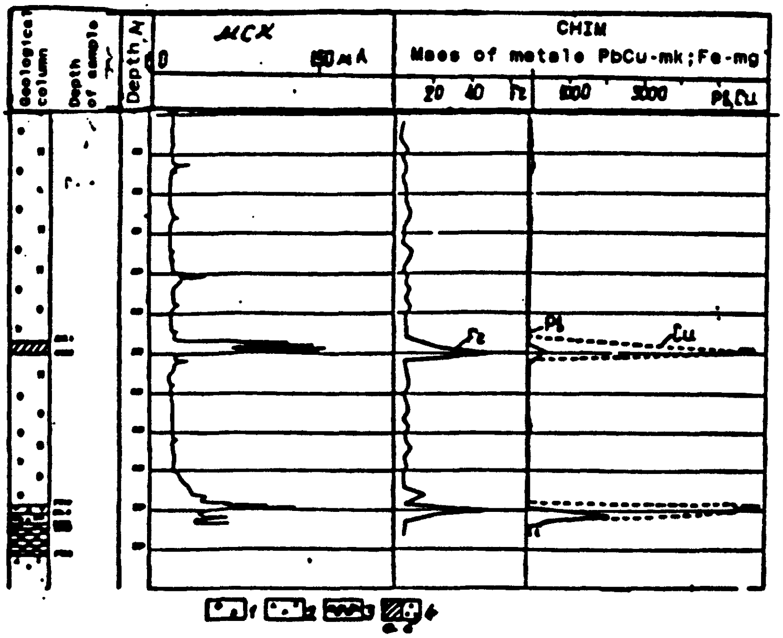


Fig. 18. Results of observations using the CHIM method in the logging version: 1) albitized rhyolite-porphyry, 2) diorites, 3) siltstone, 4) pyritic-polymetallic ores: a) vein-disseminated, b) disseminated.

## 8. ORGANIZATION AND DESIGN OF OPERATIONS

8.1. A CHIM team is normally a part of an exploration team (expedition). The qualifying number of team members is regulated by "Standards for Work Hours Necessary for Field Operations Using Contact Method of Polarization Curves and the CHIM Method", Moscow, VIEMS, 1975, 48 pp.). The total number of personnel in the field team is 10: a team chief, chemist, three senior technicians, three mechanics, a driver, and a laborer.

The team chief directs the activities of the entire team: he determines the site for the camp, the placement of the station, and the positions of the sampling profiles or intervals downhole. He supervises the set-up of the ERs and determines the regime of station operation (electrochemical extraction); he interpretes the sampling data, writes a summary based on the results of the operations, and is responsible for safety of the operation.

The chemist conducts baseline and control chemical analyses, makes sure the reagents (acids, distilled water, and others) are chemicly pure and the laboratory glassware is clean. He also oversees the thoroughness of the ER cleaning process, etc.

The senior technician (operator) sets up the ERs and other stationary equipment on the profile, controls the electrochemical extraction process, and performs sampling.

The mechanic ensures the operation of the diesel-electric assembly, performs on-going and preventative maintenance on the assembly, and participates in setting up of the station and dismantling the operations.

The driver operates the truck with the station and the trailer, and also performs the repair and maintenance of this equipment. He participates in setting up and dismantling of the station, and also participates in the organization of living conditions for the team during field operations.

The laborer takes part in the setting up and dismantling of the station and performs other related manual duties.

8.2. The entire team participates in the setting up and dismantling operations. Two persons facilitate the process of the electrochemical extraction and the station operation: the senior technician and the mechanic. When the set-up part is completed, and the station is ready to begin the work included in the aureole version of observations, the team chief establishes the regime of operation: senior technicians and mechanics are present on a twenty-four hour basis in three shifts; the chemist, the driver, the laborer and the team chief are present at one shift, taking into account expediency necessary for sampling of the ERs and performance of the chemical analyses. The operation is similarly organized during logging observations. However, in order to speed-up hoisting operations and sampling, the driver, laborer and the team chief himself can be scheduled to appropriate shifts.

The change of shifts is recorded in a separate journal. The team chief establishes regulations for work and rest, and outlines each employee's responsibilities, including camp chores. If the duration of the operations exceeds a work week, days off are made available to the workers of the team after the completion of the field project and return to the base camp.

As materials (lubricants, technical-grade and distilled water, food staples, etc.) are used up, their stocks are periodically filled from the base camp according to a schedule written up by the CHIM team chief.

8.3. The volume of investigations using the CHIM method is projected according to the generally accepted norms and according to "Typical Standards of Productivity for Field Operations using the Contact Method of Polarized Curves and the CHIM Method."

The problems, the methodologies for their solution, and the sequence of observations using CHIM for drilling, geophysical, and geochemical operations are indicated in the project. It is necessary to foresee possible reallocations of drilling and other geological-developmental operations in cases when the CHIM data are unfavorable and indicate that proceeding further with an operation is inadvisable.

Taking into consideration the novelty of the method, time should be allowed to experimentally establish regimes of extraction for the elements. The amount of research time will be determined by the accumulated experience in applying the method to each specific region.

The total expenditure can be calculated on the basis of the projected volume of sampling (given in linear kilometers when making observations in the aureole version and given in linear meters of borehole when making logging measurements). The number of crew-shifts during the extraction itself and during preparatory and dismantling stages is based on the established extraction regime. The composition of the team, cost of the materials, depreciation, and other expenses determine the cost of a crew-shift. On the basis of this cost and the number of crew-shifts necessary to complete observations on a particular area, the total expenditure for application of the CHIM method at a given area is calculated.

Figure 14

Work site______________________________ Start___________________________

Profile________________________(in aureole version)

Borehole #____________________(in logging version)

Sketch of profile location

| Measurements | Date | Time | Total current in A | Total voltage in V | Numbers of ERs |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | 1 | 2 | 3.... | 28 |
| Station on |  |  |  |  |  |  |  |  |
| Intensity V/m |  |  |  |  |  |  |  |  |
| Currents in ER |  |  |  |  |  |  |  |  |
| Currents in ER |  |  |  |  |  |  |  |  |
| Station off |  |  |  |  |  |  |  |  |
| Volume of leached material, in mcg: Pb |  |  |  |  |  |  |  |  |

Figure 14. Field journal of observations using the CHIM method in the aureole or logging version.

Figure 16

| # | Date | Work site (borehole, profile) | # of ER and # of sample | Sample volume, ml | Element | Aliquot sample in ml | Elem. conc. aliquot solution mcg/ml | Element's mass in ER, in micrograms |
|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |

Figure 16. Journal of results of chemical analyses on PEC.

Journal of results of chemical analyses on FPL-1 has two additional columns: 10) Analysis regime and 11) Current in mcA.

## Appendix I

### Materials and Tools Required for Field Applications of the CHIM Method.

| | Item | Amount | Purpose |
|---|---|---|---|
| 1. | Distilled water (metal-free) | 5 l | To prepare solutions in 30 50-ml volume ERs & to wash them |
| 2. | Nitric acid, $HNO_3$, c.p. | 0.5 l | Same |
| 3. | Porcelain jug, 1 l | 1 | To prepare acid solution |
| 4. | Measuring glass (cylinder), 1 l, glass or plastic | 1 | Same |
| 5. | Funnel, 0.5-1.0 l glass or plastic | 1 | Same |
| 6. | Test tubes, 50-100 ml, glass or plastic | 30 | To remove solution samples from ERs |
| 7. | Sticks, gl.or plast. | 2 | To stir solutions |
| 8. | Basin, 5 liter polyethyl. | 1 | To wash ERs |
| 9. | Plastic bags | 2-5 | To store ERs & parchment |
| 10. | Pear-shaped bottle, 50-100 ml, with a spout | 2 | To remove solution samples from ERs |
| 11. | Glass (beaker), 0,5 l | 1 | To wash # 10 |
| 12. | Plastic wrap | 0.1 $M^2$ | To cover test tubes |
| 13. | Elastic nipples (pacifier-like) | 5 | To cover test tubes (externally) |
| 14. | Gloves, rubber | 2 pairs | To work with acids |

| | | | |
|---|---|---|---|
| 15. | Titanium (carbon) electrodes | 30 | For use in ERs |
| 16. | Parchment (GOST 1341-69) | 0.2 $M^2$ | To prepare membranes for the ERs |
| 17. | White adhesive tape | 1 roll | To mark test tubes |
| 18. | Shears | 1 | |
| 19. | Short stick made of steel with a butt end D = 28 mm | 1 | To knock out membranes |
| 20. | Measuring tape | 10 M | For laying of the profile |
| 21. | Compass | 1 | Same |
| 22. | Protractor | 1 | Same |
| 23. | Straightedge | 1 | Same |
| 24. | Table knife | 1 | Breaking in the hole under the ER |

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Issue No. 223

Manual

# THE EXPLORATION OF ORE DEPOSITS BY THE CHIM METHOD

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# FINDING BURIED GOLD MINERALIZATIONS

S. G. Alekseyev and I. S. Goldberg

The problem of finding a buried gold mineralization arises in several situations, typically, during 1) exploration of the flanks of known deposits; 2) in the process of prospect evaluation; 3) in correlating of ore zones uncovered in neighboring areas but separated by alluvial cover. It becomes all the more important the richer the discovered portion of the mineralization is and the more promising the undiscovered portion of a gold deposit appears to be. Tracing gold mineralization takes on a special significance when exploring covered areas. In such areas significant amounts of drilling can be used up. This is especially true in districts with complex geology and complicated ore grade distribution. This article discusses testing of the CHIM method to determine whether it is an easier method than drilling for tracing gold mineralizations under unconsolidated overburden.

The survey area is classified as a poorly exposed; 30-40% of the area is covered with transported unconsolidated overburden up to 70-100-m thick. Since such overburden is not ubiquitously present, the task of finding gold-bearing outcrops and subcrops is facilitated by the geological mapping on the scale of 1:50,000 and smaller, and surface geochemical surveys. Gold-oriented soil geochemistry is usually used.

Gold prospects and/or zones of mineralization are trenched and, in completely covered areas, they are drilled. The drill grid is usually 200x20-40 m with an average depth of 50-70 m.

In the area of the CHIM testing, the sedimentary formations are mainly represented by sandstones and siltstones. The rocks are graphitized to a significant degree, and thick, deep zones of chemical weathering and oxidation develop within them. The ore-hosting structures are tectonic zones striking north-west and dipping north-east. The primary ores are silicified sulfidized sandstones and siltstones. The gold in the primary ores exists in the form of admixtures in pyrite and arsenopyrite; a small amount of free gold is also present. In the supergene zone, the primary ores were completely oxidized. According to the fire assay and metallurgical test data, all of the gold in the oxide orebodies exists as a free gold. The oxide orebodies occur in a linear belt and are of significant width and length. The contacts of the orebodies are indistinct and can be mapped only on the basis of assay data.

It was shown before [1] that similar ore bodies and zones of gold mineralization can be delineated by the CHIM method if the thickness of unconsolidated overburden is about 20-m. The survey was conducted under the following conditions. Gold was extracted at element-receivers (ERs) with large membrane areas, 40 $cm^2$, in a high-power regime (300-400 A through each ER) at an average electric field strength of 2 V/cm. The extraction time was 10 hours. The element-receivers were distributed along the profile at steps of 7.5 m. The contents from four element-receivers were grouped into a single sample so the quantity of extracted gold will exceed the minimum amount necessary for analysis. This method successfully delineates a gold mineralization by outlining anomalies with amounts of gold exceeding 0.01 ppm. The anomalies are satisfactorily reproduced during repeated observations and are spatially distributed directly above the tops of the ore bodies. Mineralized zones with noncommercial gold concentrations are characterized by anomalies with less than 0.1 ppm. They are not always reproducible during repeated observations, since the quantity of gold extracted within such anomalies is too near the limit of sensitivity for the analysis (0.003-0.005 ppm).

The proposed methodology for CHIM was used to trace gold mineralizations at two gold prospects in Eastern Kazakhstan.

Prospect I (Fig. 1). The exposed portions of the area contain several zones of mineralization. High gold values were found in several of them on the basis of individual samples. The zones are "lost" under unconsolidated overburden 50-70 m thick. They can be outlined by the CHIM method. The profiles and their relationship to the zones on outcropped hills is shown in Fig. 1. Three levels of gold extraction were established on the basis of the results. The most intense extraction is characterized by masses of more than 0.01 ppm. These are first-order anomalies; they were found on profiles 58, 66, 67, and 72. The anomalies were spatially combined into three anomalous zones, which have been named the Northern, Southern, and South-western zones. The Southern zone can be traced from the east to the west along several profiles. Its width is 62 m on Profile 72. Further to the west, it can be traced through Profile 67, where it reaches a width of 100 m. On an outcropped portion of the area between these two profiles, the zone is visible in mine workings, and it is intercepted in drill holes. Thus, a zone of mineralization found in the outcropped part of the prospect can be traced from the south to the west and to the east. In the west, it tapers out or the gold values within it diminish. To the east, however, the zone extends further than Profile 72.

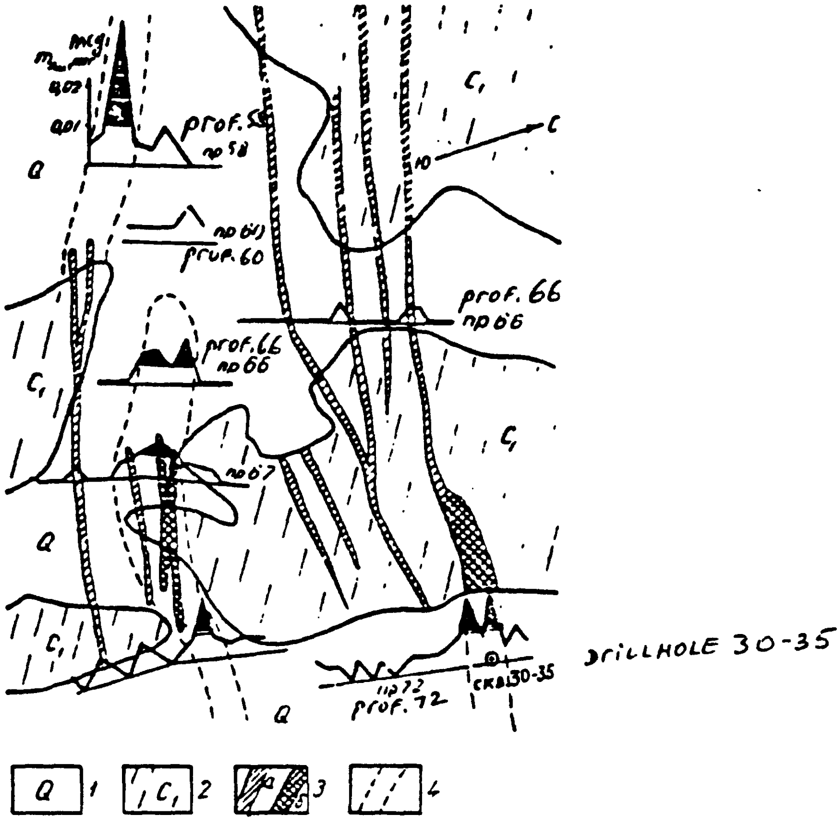

Fig. 1. Results from exploring the ore zones using the CHIM method. Prospect 1: 1) Quarternary unconsolidated; 2) Early Carboniferous sandstones and siltstones, 3) zones with noncommercial (a) and commercial (b) mineralization, 4) gold zones traced by the CHIM method.

To the south, the Southern zone abuts the Southwestern zone, which is noted on Profile 58. The Southern zone is confirmed here in an outcropped area which is also trenched. The zone continues to the east, where it can be traced by a weak CHIM anomaly. It can then be traced by trenches at a next outcrop and, still further to the east, again by a weak CHIM anomaly on Profile 72. It is necessary to note that the CHIM anomalies above the Southwestern zone are weak, with the exception of the anomalies in the western portion. This correlates with the small gold content in the outcropped portion of the zone.

The Northern zone is clearly delineated only on Profile 72. Its width is 100 m. The continuation of the zone to the west is apparently a zone of mineralization mapped and sampled in mine workings in the exposed portion of the area. Still further to the west in the area of Profile 66, according to the data from the CHIM method, the ore zone either tapers out or the gold values within the ore zone decrease significantly.

Thus, the anomalous zones which most probably contain gold mineralization within their contours can be traced at Prospect I using the CHIM method. The results of the CHIM operations at present are being verified along the Northern zone (Profile 72), where a zone of mineralization with an ore grade of gold was established by drillhole 30-35 (see Fig. 1) in the core of the CHIM anomaly.

Prospect 2 (Fig. 2). Several gold-bearing zones were discovered. A portion of these contain high grades of gold in the trenched part of the prospect. The CHIM results were obtained in the western and eastern parts of the area along four profiles in order to discover the extension of the zones under unconsolidated overburden. The thickness of the latter was 30-50 m.

According to the CHIM results, the major zones with commercial gold mineralization do extend beneath the unconsolidated areas. A zone exposed by trenches can be satisfactorily traced on Profiles 2 and 1 in the northeastern flank of the area. It apparently continues further in a southeasterly direction. This same zone extends to the northwest through Profile 4.

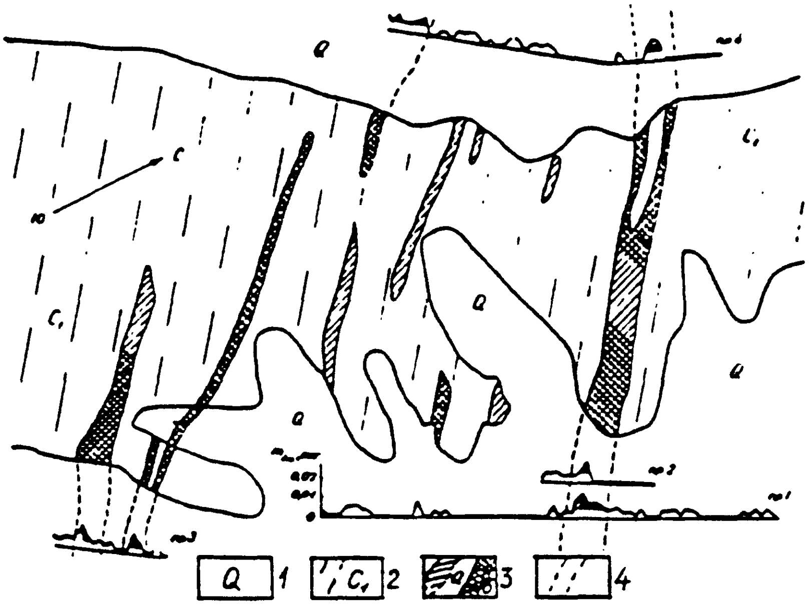

Fig. 2. Results from tracing gold mineralization using the CHIM method. Prospect 2: 1) Quarternary unconsolidated; 2) sandstones and siltstones ($C_1$), 3) zones of mineralization with low-grade (a) and commercial (b) mineralization, 4) ore zones traced by the CHIM method.

In analogous fashion, we can trace zones exposed in outcrop in the southeastern part of the area; they register well in the CHIM anomalies along Profile 3.

Still another anomalous zone extends into the northern part of the area cross-cutting the southern end of Profile 4. This zone has not been contoured and has a lower gold content than the other zones.

Besides the described first-order anomalies, the other weakly anomalous areas with 0.005-0.008 ppm extractions of gold were found on all of the profiles. Their lesser intensities indicate that, although gold values within such anomalies are higher than in the bedrock, the gold content at these sample sites is too low-grade.

We have discussed examples of tracing gold mineralization in the areas of low topography filled with unconsolidated Quarternary deposits. These examples illustrate the promise of the CHIM method. At the prospects surveyed by CHIM, the delineation of mineralized zones allowed us to decrease the amount of drilling by up to 60% as compared with the drilling needs predicted initially without the use of the CHIM method. We should add that tracing of the zones of gold mineralization at the two prospects mentioned took 1.5 months and significantly accelerated the exploration of these prospects.

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# CHIM SURFACE SET-UP FOR UNIPOLAR EXTRACTION.

Yu. S. Ryss and I. S. Goldberg.

In the set-ups shown on Figure 3, the auxillary grounding electrode is moved out of the survey area (to "infinity"). The primary ground is a system of element-receivers placed at points of intersection of concentric circles with radii or at points of intersection on a rectilinear grid of profiles. The dimensions of the grounding electrode are selected in accordance with the given depth of investigation. Depending upon the distribution of current flowing from the various ERs and the distance between ERs within the ground, the structure of the field within the volume of rock can be selected to be either homogeneous or central or of another type.

A set-up of the type involving a charged body differs from others in that the auxillary grounding is placed within the target object using boreholes or mine workings.

Surface set-up for bipolar extraction. In this set-up, the auxillary electrode is equipped with an ER, just as the primary ground is. Both grounding electrodes are arranged along the strike of the studied zone at a distance from one another which is determined by the actual goals of the study.

The circular "aureole" set-up consists of a central ER and an auxillary circular ground surrounding the ER. The volume being worked is determined by the size of the circle. When investigating aureoles, the radius of the circle usually amounts to 0.5-1 m.

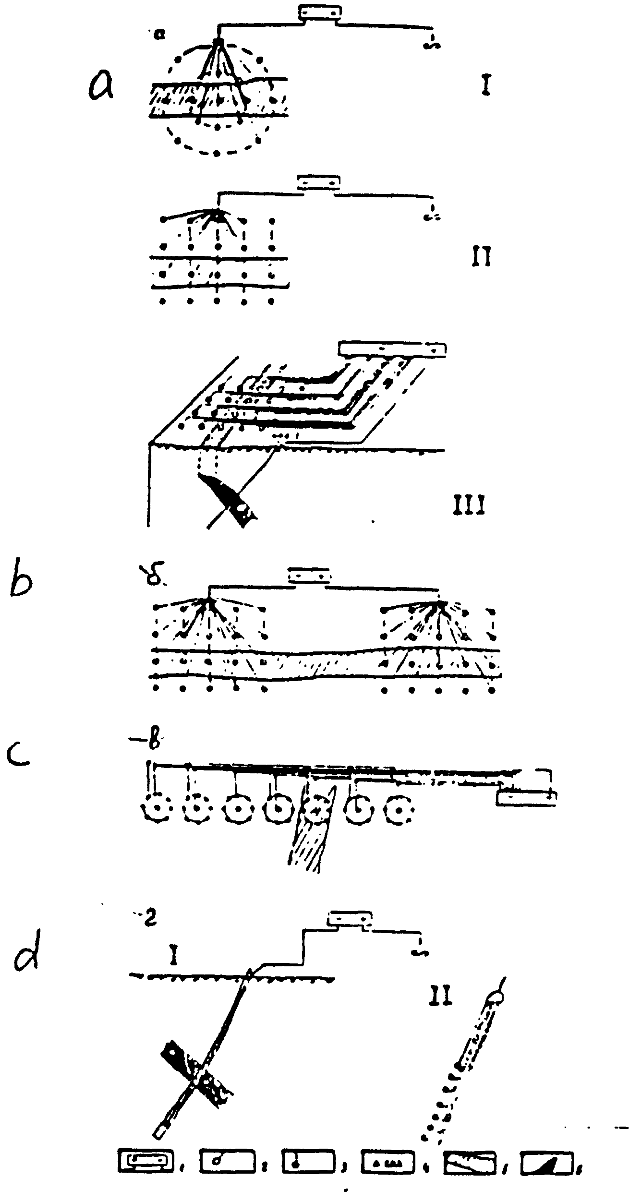

Fig. 3. Diagram of field set-ups in the CHIM method: a)surface set-up for unipolar extraction of metals (I: circular, II: rectilinear, III: by means of a charged body), b) surface set-up for dipole extraction of metals, c) "aureole" circular set-up, d) logging set-up (I: overall scheme, II: braided cable); 1) power source, 2) element-receivers, 3) auxillary electrodes, 4) boreholes, 5) projections of mineralized zones at the surface, 6) ore bodies.

In the Logging set-up, the primary ground takes the form of a chain (garland) of ERs lowered into the borehole on a multiple cable. The auxillary electrode is placed either in "infinity" or on the surface at the borehole opening (casing pipe can be used).

Observations using CHIM in "aureole" version are the simplest. Circular surface set-ups by 20-30 pieces hooked up in parallel to the source are usually used. Set-ups are positioned along a profile or over a specified area. The ERs are joined to the negative pole of the power source, and the circular auxillary grounding electrodes are joined to the positive pole. One can use batteries of accumulators, rectifiers of alternating current, electromechanical assemblies, and other equipment with the power of 1 kilowatt or more as current sources. Electrical current is passed through the ERs for 1-2 days with periodic or one-time testing of the ER contents. In order to provide identical extraction conditions at each set-up within the circle, measurements of the electric field strength are made at specific points. The electric field strength is selected for all of set-ups at the site under investigation by varying the current passing through individual set-ups. The analysis of the contents of the ERs is carried out either by extraction of the solution or directly within the solution with the aid of chemical or various types of physico-chemical analysis.

Determinations of the metals present in the aureole, their relative quantities, and the positions of ore-bearing zones are usually involved in the "aureole" version of the CHIM method. Taking into account the linear character of the dependence of the first branch of the accumulation-vs-time curve, graphs along the profiles under investigation are constructed with respect to the magnitude of dm/dt or values of m for a fixed t.

In Fig. 4, results are presented for extraction of nickel, copper, and cobalt at one of the copper-nickel deposits of the

Kola Peninsula. The mineralization is hosted by amphibolites interbedded with granito-gneisses and intruded by plagio-microcline granites. These rocks are covered by glacial moraine 8-12-m thick. Surface geochemical sampling established that the overburden has more or less identical concentrations of trace elements. No aureole was found above the mineralization. Electrochemical extraction from small surface set-ups 1-m in diameter resulted in the accumulation of mobile forms of nickel, copper, and cobalt at the ERs after current was passed for two days. Directly above the top portion of the mineralization, 150-200 mcg[1] of nickel was leached (in 2 days); above the buried portion and also outside the orebodies under the same conditions, 20-25 mcg of nickel were leached. Copper and cobalt were leached in quantities of 40-45 mcg above the mineralization and in quantities of 10-15 mcg at a distance from its upper portion. Thus, within the near-surface horizon of overlaying rocks, dm/dt, and, correspondingly, the contents of nickel, copper, and cobalt, are greater above the hanging wall of the mineralization than along both sides of the mineralized zone. During electrochemical extraction, an aureole was discovered above the mineralization which had not been identified on the basis of bulk sample analysis during the geochemical survey. The difference in discovering the aureole by total sample concentration or by electrochemical extraction is due to the fact that the electrochemistry facilitates the accumulation and selective determination of mobile forms of elements. These mobile forms apparently constitute a fraction in relation to other fixed forms. The masses of the fixed forms are greater than the masses of the mobile elements and are homogeneous over most of the profiles (and, apparently, within the area as a whole. The small changes in the amount of an element that are found during the bulk analysis go practically unnoticed. At the same time, such changes can be recorded very clearly in terms of their

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[1] mcg = microgram

intensified accumulations when using the CHIM method.

When using geochemical extraction, similar effects associated with the detection of covered aureoles can be observed in other areas. The profile of a polymetallic deposit is presented in Fig. 5. The ores here occur in a quartz-sericite altered zone covered by loose clay-rich overburden 40-50 m in thickness. According to the results of a soil survey, background concentrations of lead and copper are less than 10 ppm. During geochemical extraction from the same set-ups used at the preceding site, an aureole with a maximum extraction of lead reaching 90-110 mcg and a maximum extraction of copper reaching up to 360 mcg can be detected above the ores. Lead values of ~50 mcg and copper values of ~50-65 mcg were detected on the flanks of the deposit.

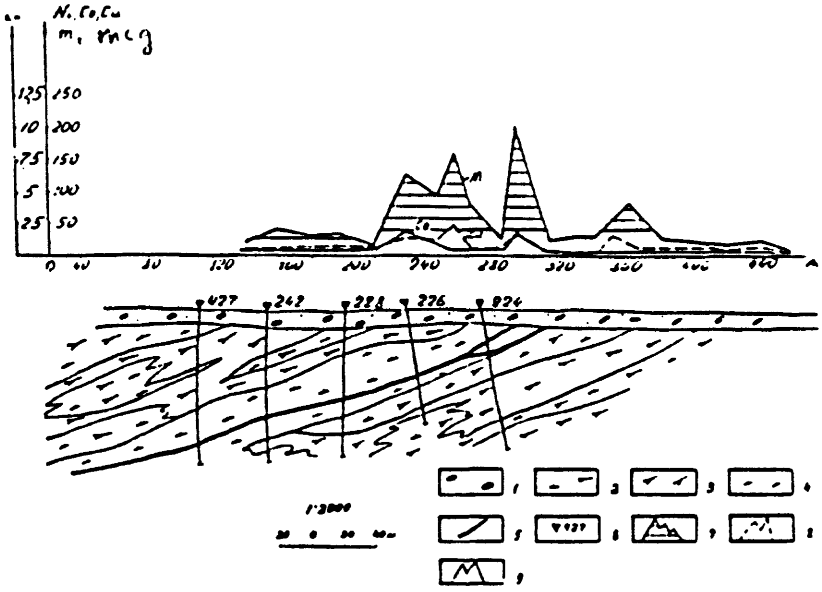


Fig. 4. The CHIM results for a copper-nickel deposit (Kola Peninsula): 1) moraine, 2) plagioclase-microcline magmatitic gneiss with amphibolite, 3) plagio-microcline granite, 4)feldspar amphibolite, 5) ores, 6) boreholes, CHIM graphs: 7) nickel, 8) copper, 9) cobalt.

On Fig. 6, we show an aureole detected during geochemical extraction under still more complicated conditions than those described above. The polymetallic mineralization occurs within volcano-sedimentary chloritized rocks covered by clays ~100-m thick. The mineralization itself does not subcrop under the overburden and occurs below the bedrock contact at a depth of 20 m. As is evident from the figure, 20-25 mcg of lead and 15-20 mcg of copper was leached above the upper portion of the ore. Outside the ore zone, 5-10 mcg of lead and copper were extracted.

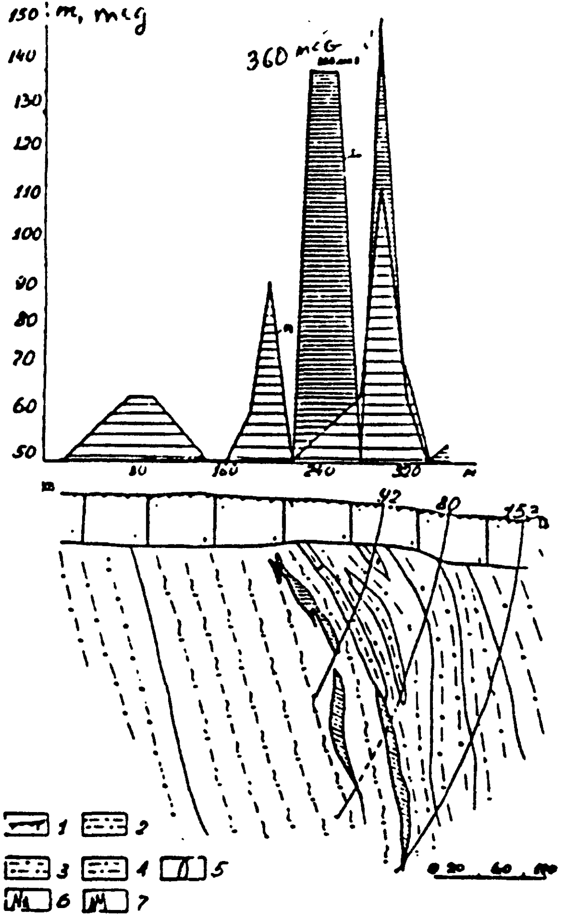


Fig. 5. Results of the CHIM method at polymetallic deposit I (Rudnyi Altai Mts.): 1) unconsolidated deposits (clays, loams), 2) schistose dioritic porphyries and microdiorites, 3) basalts, 4) sericite-quartz schists, 5) polymetallic ores, CHIM graphs: 8) lead, 9) copper.

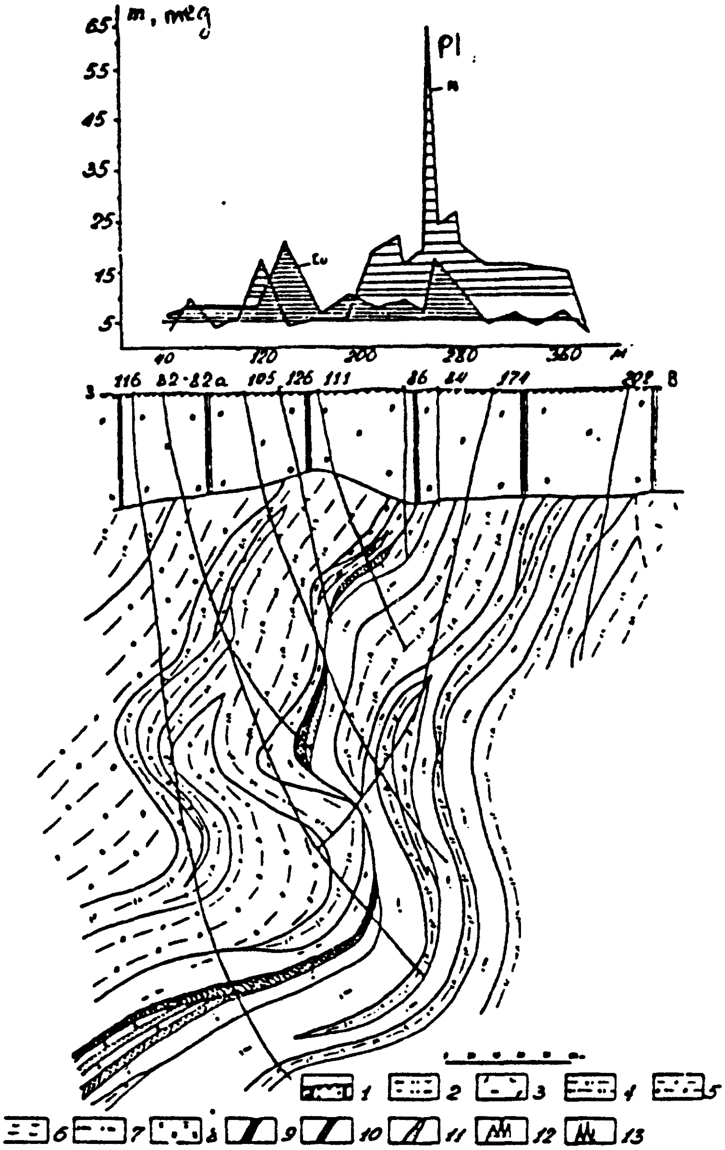


Fig. 6. Results of the CHIM method at a polymetallic deposit (Rudnyi Altai Mts.): 1) unconsolidated deposits (clays, loams), 2) siltstones, sandstones, tuffs, 3) tuffs of andesite composition, 4) tuffs of silicic composition, 5) basalts, 6) chloritized tuffs, 7) silicified mudstones, 8) disseminated polymetallic ores with chlorite, 9) massive copper-pyrite ores, 10) massive polymetallic ores, 11) veined-disseminated ores, CHIM graphs: 12) lead, 13) copper.

The results at the sites mentioned and also observations at other sites lead to the conclusion that geochemical extraction in the "aureole version" allows one to detect weak aureoles not identifiable by bulk content of elements. As a result, the "aureole" version of the CHIM method broadens the possibilities of geochemical surveys and permits the investigation of areas in which it would be difficult to conduct the soil surveys. Those are covered areas and also areas with weakly developed supergene processes. Existing results indicate the possibility of detecting geochemical aureoles of mineralization when the overburden thickness is ~100 m. This depth is apparently not the limit. It can be anticipated that, by changing the electrical parameters and also the extraction time, significant accumulations can be achieved in areas with greater overburden thickness.

The detection of geochemical aureoles of deep-seated mineralization by using the geochemical extraction indicates a migration of ore elements in mobile forms upward through unconsolidated overburden. As can be seen, these elements migrate significant distances. Taking into consideration that unconsolidated overburden, especially the moraines (the Kola Peninsula), is transported to the site of an ore deposit from afar, one can conclude that the anomaly is generated by the penetration of elements through a sequence of rock rather than the formation of mobile forms as a result of a dispersal of primary mineral fragments. Comparatively limited periods of migration cause the geochemical aureoles to be continuously fed and cause elements to accumulate near the surface. These features are two important characteristics of the "aureole" version of CHIM as a method of exploring for ore deposits. One of these characteristics consists in the fact that ore zones can be detected through allochthonous overburden material (eolian sands, moraine, mudflows, etc.) by using the "aureole" version of CHIM. Such overburden, at present, is a serious impediment to geochemical surveys based on total sample composition. Another feature of the "aureole" version of CHIM is that it can utilize precisely the mobile forms of elements, i. e., those forms which have come from the depth. Thus, aureoles detected on the basis geochemical extraction are more directly associated with ore zones than the aureoles found on the basis of total content.

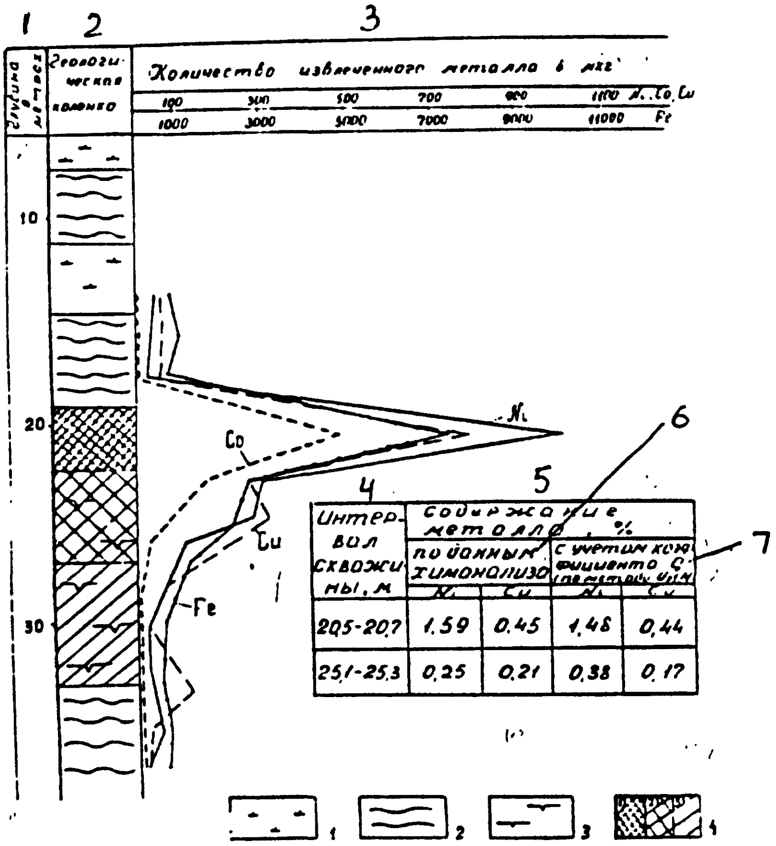
The distribution of the total content can fluctuate not only depending upon migration processes but also depending on whether an element occurs in the lattice of a mineral.

The 'aureole' version of CHIM can be used, as can any other geochemical method, to test geophysical anomalies. As is well known, zones of conductivity are often represented by pyrite, pyrrhotite, and, more rarely, by polymetallic copper and copper-nickel ores. The detection of geochemical aureoles of high copper, lead and nickel on anomalies discovered by electrical geophysical methods substantially increases the chance of finding an ore deposit. On the other hand, an absence of geochemical aureoles can serve as a sign that the geophysical anomaly is not related to mineralization.

The 'aureole' version of CHIM proves useful in detailed exploration of deep-buried deposits and in testing of geophysical anomalies. Nevertheless, a basic shortcoming of any geochemical method remains in this CHIM method as well. The problem we are talking about is an inability of a geochemical method to evaluate the grade of an ore mineralization. A future 'fundamental' version of CHIM will permit one to record both the initial and the subsequent branches of the geochemical curve of accumulation vs. time (hodograph) which would help to overcome the problem.

The research in this direction is still in the early stages. An important inhibiting factor is the uncertainty associated with our conception of the velocities or mobilities of ions movement in rocks. Investigation of the mobilities of ions in various media [2, 3, 4] showed that mobility varies from thousandths to thousands of $cm^2$/volt-hour. The observed variations are caused by many factors which are extremely difficult to quantify. These include: the composition and concentration of pore solutions, the structure of the pore space, the composition of the solid phase, electrokinetic phenomena, etc. The totality and variety of effects of different factors makes experimental set-ups complex and lead to an uncertainty with respect to experimental results on account of one or another factor. It is quite obvious that practical implementation of the "fundamental" CHIM version is possible in cases involving high mobility values. The conditions under which the mobility of ions in rocks exceeds units of cm$^2$/volt-hour are not yet well known. Further studies and field experiments are needed in this direction.

The "fundamental" or "primary" version of CHIM is comparatively simple to implement during logging of a borehole. The close proximity of the element-receiver to the borehole walls allows to dissolve minerals from the borehole walls and accumulate elements at the element-receivers under a small electrical exposure over a brief period of time. A complete geochemical curve of accumulation vs. time for each element-receiver permits one to estimate the content of elements in the rock and to construct the downhole distribution curves of element concentrations for different depths. A qualitative concept of such a distribution can be achieved if we record the change in the mass m leached downhole over a fixed period of time corresponding to the branch of the accumulation-vs.-time curve. This qualitative concept would reveal any enriched intervals and show their pattern relative to one another. The results of the CHIM logging at one of the boreholes (Kola Peninsula) are presented in Fig. 7. As is evident from the figure, the ore interval at a depth of 20-21 m is well determined by high extraction of nickel, copper, cobalt, and iron against the low background associated with the extraction of these same elements in the host rock. Copper and nickel gradually decrease downward in the peridotite sequence and then abruptly decrease at the transition from ores to the underlying phyllites. At the point of maximum (20.5-20.7 m) of the extracted quantities of nickel and copper and at a depth of 25.1-25.3 m, we determined in the laboratory the contents of the indicated elements in ores and in mineralized peridotites and calculated empirical Q coefficients. A comparison of values found on the basis of the CHIM results and the laboratory analysis of the core indicates that they are satisfactorily similar. It follows that evaluation of the elements content on the basis of the CHIM data is quite realistic.



| Интервал скважины, м | Содержание металла, % | | | |
|---|---|---|---|---|
| | по данным химанализа | | с учетом коэффициента Q (по методу ЧИМ) | |
| | Ni | Cu | Ni | Cu |
| 20,5-20,7 | 1,59 | 0,45 | 1,48 | 0,44 |
| 25,1-25,3 | 0,25 | 0,21 | 0,38 | 0,17 |

Fig. 7. Results of logging using the CHIM method (copper-nickel ores): 1) amphibolites, 2) biotite gneisses, 3) peridototites, 4) nickel content: 1) 1%, 2) 0.5-1.0%, 3) >0.5%.

Key: 1) Depth in meters, 2) Geological column, 3) Quantity of leached metal in mcg. 4) Interval of borehole, m, 5) Metal content, %; 6) Chemoanalytical data; 7) Taking coefficient Q into account (according to the CHIM method).

The sound principles of the CHIM method and the successful experience at applying the method offer several possibilities of using the chemical leaching for exploration and for economic geology. Deep-seated ore deposits covered with unconsolidated overburden up to 100-m in thickness can be detected by using the "aureole" version of the CHIM method. It is also possible to discover zones of mineralization through transported overburden. In the logging version, the CHIM method permits to determine the downhole distribution of elements and to determine the grade in certain beds of interest. In principle, it is possible to leach metals directly from deep ores. This problem is still in the initial stage of investigation.

# PATTERNS OF ELECTROCHEMICAL LEACHING OF ELEMENTS IN THE SIMPLEST PHYSICO-CHEMICAL SYSTEMS
## (Report I)

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The electrochemical extraction of elements from rocks, the process upon which the CHIM method is based [1], consists of a combination of many interconnected phenomena: the solution of concentration and chemical conversion of components around the electrodes through which the electrical current is introduced into the rock, etc. In order to more thoroughly investigate phenomena which are interactive and simultaneously dependent upon many controlling factors associated with the process and also in order to begin to manage these phenomena, it is advisable to study the totality of these processes, beginning with the simplest physico-chemical system and then moving to more complex systems gradually approximating actual rocks.

The simplest model for electrochemical extraction of elements is a two-chambered cell containing different media separated by a membrane. Electrodes placed in the chambers introduce an electrical current into the system from an external source. All of the processes characteristic of electrochemicalextraction take place in such a model: the current passing through dissolves and transforms minerals, and ions are displaced and concentrated around the electrodes. By lowering the intensity of the current and the time of its operation, one can vary the intensity of the electrical action. Changing the composition of a medium allows one to investigate the effect of a current as well as effect of a texture and structure of the rock upon electrochemical extraction. Finally, changing the composition of the electrodes allows one to investigate the effect of the composition of the electrode reactions, which is especially important at the sites where the elements are concentrated - at the element-receivers (ERs). Actually, one chamber in the proposed model can be considered an element-receiver; the other is a simulation of the surrounding medium. During the time the processes are taking place, but while products of the electrode reactions have not yet arrived to the ER from the second supply electrode from the chamber simulating the surrounding medium, the results of the investigation correspond to phenomena taking place in the environment of the ER during CHIM surveys in the aureole version [1]. When products of electrode reactions from the second electrode arrive at the ER simulator, on the other hand, the phenomena observed correspond to the extraction of elements directly from ores. This manner of extraction is utilized during CHIM operations in general and in the logging versions.

The simplest model examined here has its applications in a study of various factors controlling the electrochemical extraction of elements. In the present article, we characterize the role of the acid in the element-receiver and its effect upon the intensity of the extraction and the reproducibility of observations using the CHIM method. Other results will be presented in subsequent reports.

As is well known [1], acid is introduced into element-receivers in order to neutralize OH- ions arising during the cathode dissociation of water. This is because the OH- ions move toward metallic cations approaching the ER and block their approach to the ER. In addition to neutralizing OH- ions, the acid present in the ER unavoidably results in the diffusion of acid into the surrounding medium. This has two negative consequences. In the first place, hydrogen ions removed from an element-receiver by the electrical current are turned back to the ER. In this way, the portion of current deployed for the transport of useful components is decreased. In the second place, hydrogen ions turning up in the rocks around the ER can cause dissolution of the rocks and can add recently dissolved components to the extracted elements, thus distorting the results of the strictly electrochemical extraction of elements.

Since the current action impedes the diffusion of hydrogen ions from the element-receiver, apparently one can select conditions for carrying out the processes under which hydrogen ions will not leave the range of the ER. Experimental and numerical simulation approaches can be used to solve these problems. The results of investigations using both approaches are presented below.

A diagram of the electrochemical cell in which the investigations were conducted is shown in Fig. 1. The cell consists of two chambers separated by a membrane (10). Chamber (4) simulates the ER and chamber (3), large in size, simulates the external medium. A platinum anode is placed at the butt-end of chamber (3) and a titanium cathode is placed at the butt-end of chamber (4). In order to decrease the convection of the solution, chamber (3) is partitioned by three membranes which, as in the case of the ER membrane, are cellulose films 80-mcm in thickness.

The cell is connected to a stabilized source of direct current which remains unchanged during each experiment. The observations are made in the form of geoelectrochemical accumulation-time curves (hodographs) [1]. After electrical current has been passed through chambers (3) and (4), the solutions filling the chambers are removed. The titanium electrode is washed off with hydrochloric acid (1:1). The quantities of the participated in the experiment elements in the solution are then determined.

Solutions of nitric acid, forming easily dissolved compounds with the majority of metals, were selected as the medium in the ER. This allowed elements to accumulate at the element-receiver.

Solutions of zinc sulfate were chosen for the simulation of the external medium: zinc ions do not interfere with the determination of nitrate ions in the samples (nitrate analysis is necessary in order to construct a complete balance for all carriers of current; moreover, there is a fast and sensitive methodology for zinc determination).

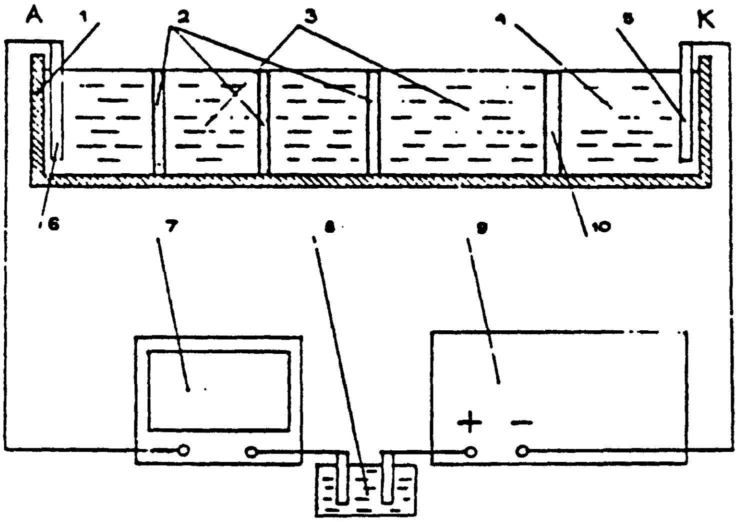

Fig. 1. Diagram of set-up for conducting the experiments: 1) electrochemical cell, 2) membrane on the anode side, 3) chamber simulating the external medium, 4) chamber simulating the element-receiver, 5) titanium cathode, 6) platinum anode, 7) ammeter, 8) coulombmeter, 9) direct-current source, 10) membrane of element-receiver.

The concentration of zinc was determined by a photocolorimetric technique using sulfarsecene on a FEK-56m instrument [5]. The control was implemented by polarographic technique on a FPL-1 instrument [1]. Both methods yielded results within margins of error not exceeding 10%. The concentration of nitrate ions was determined by the photocolorimetric method with phenoldisulfoxic acid [2]. It was first established that zinc lowers the values determined for quantities of nitrate ions at concentrations $Zn^{2+}:NO_3 = 300:1$ or more. Therefore, corrective coefficients obtained for reference solutions were introduced when determining $NO_3^-$ in solutions with high concentrations of zinc. The concentration of hydrogen ions was measured by titration with a deci-normal solution of sodium hydroxide with methyl-orange indicator. The error of the analysis (coefficient of variance) was 10% for the control analysis of samples. The total volume of the control analyses was no less than 25-30%.

The effect of the concentration of acid in the ER upon the extraction of zinc was investigated in several sequential stages. First, a reference time for carrying out all experiments was established. This was necessary because an electrode process takes place at anode (which is placed in the external medium) involving the oxidation of OH- with the formation of hydrogen ions transported to the ER under the action of the electrical field. If the hydrogen ions reach the ER within the time of the experiment, a portion of the current will be deployed to transport them through the membrane (this results in a redistribution of the current between the other carriers). The contribution of hydrogen ions formed at the anode to the total quantity of current passing through the membrane is not subject to precise calculation, since hydrogen is present at the ER in a significantly higher concentration than that formed at the anode. It was simpler from a technical standpoint to limit the time the experiments were run, to establish a reference time when the hydrogen ions formed at the anode, still not having reached the membrane of the element-receiver and, consequently, still not having participated in transfer of current through it.

In order to determine the reference time, concentration of the zinc from a 0.1 N solution of zinc sulfate in 0.1 N $HNO_3$ was carried out at a current strength of up to 300 mA in a time interval of up to 8 hours. The results of the observations are presented in Fig. 2, where geochemical accumulation-time curves for the extraction of zinc are shown. Without current or with currents of 3, 10, or 30 mA, the increase in the mass of zinc per unit of time i.e., the rate of extraction, remains constant over the course of 8 hours. At currents of 100 and 300 mA, changes in the rate of the extraction of zinc take place at times of 5.5 and approximately 2.5 hours respectively. They are linked to the arrival of hydrogen ions formed at the anode, a fact indicated by the change in the pH value in the chamber simulating the external medium. The change in pH in the near-membrane zone on the side of the external medium shows that the acidity of the solution does not change for currents up to 30 mA, but that an acidic wave propagating from the anode reaches the element-receivers after 5.5 and 2.5 hours for currents of 100 and 300 mA respectively. We chose a reference time of 1 hour. During this time period, we studied the effect of acid concentrations in a range from 0.01 to 3 N upon the quantity of extracted zinc at current of 0 to 300 mA (TABLE 1).

For the quantity of zinc transported to the ER as a result of diffusion (without current), see TABLE 1, column 2. the current is shown in columns 3-7. The total quantity extracted (M) includes a migrational ($M_m$) and diffusional ($M_D$) components. The first component is associated with accumulation under the influence of the electrical-field gradient; the second is associated with the concentration gradient. Columns 8-2 contain data on the

migrational component, defined as the difference: $M_M = M - M_D$.

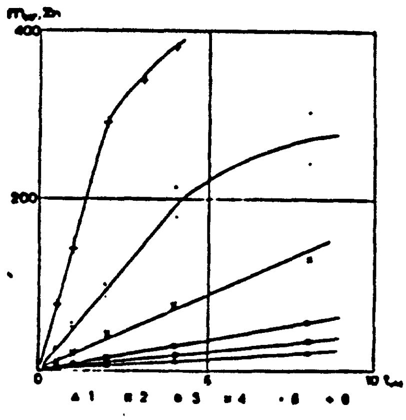

Fig. 2. Geoelectrochemical accumulation-time curves for the extraction of zinc; 10 without current; at currents of: 2) 3 mA, 3) 10 mA, 4) 30 mA, 5) 100 mA, 6) 300 mA.

For the quantity of zinc transported to the ER as a result of diffusion (without current), see TABLE 1, column 2. the current is shown in columns 3-7. The total quantity extracted (M) includes a migrational ($M_M$) and diffusional ($M_D$) components. The first component is associated with accumulation under the influence of the electrical-field gradient; the second is associated with the concentration gradient. Columns 8-2 contain data on the migrational component, defined as the difference: $M_M = M - M_D$.

(I) TABLE 1. Quantity of zinc accumulated at the ER.

| Acid concentration in ER, N | $M_D$, mg | M, Mg | | | | | $M_M$, mg | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Current strength, mA | | | | | | | | | |
| | | 3 | 10 | 30 | 100 | 300 | 3 | 10 | 30 | 100 | 300 |
| 0,01 | 1,7 | 3,2 | 6,7 | 17 | 55 | 160 | 1,5 | 5,0 | 15 | 53 | 158 |
| 0,1 | 2,7 | 4,0 | 7,1 | 18 | 46 | 143 | 1,3 | 4,4 | 15 | 43 | 140 |
| 0,3 | 4,6 | 5,0 | 5,5 | 11 | 49 | 133 | 0,4 | 0,9 | 6,4 | 44 | 139 |
| 1,0 | 9,6 | 10,0 | 10,0 | 11,5 | 17 | 135 | 0,4 | 0,4 | 1,9 | 7 | 125 |
| 3,0 | 12,5 | - | 13,0 | 13,5 | 18 | 38 | - | 0,5 | 1,0 | 5,5 | 25 |

By analyzing the data in TABLE 1, one can see that the mass of zinc increases with increasing current. The mass remains more or less high for each increase up to a certain concentration of acid. It then decreases sharply with increasing concentration of acid. With increasing current, the boundary between quantities of accumulated zinc (see TABLE 1) shifts to an area of higher concentrations: for 3-30 mA, a change in the quantities of extracted zinc occurs at 0.3 N. A change occurs at 1 N for a current of 100 mA and a change occurs at 3 N for a current of 300 mA.

The results of the experiments allow us to determine the portion of current involved in the transport of zinc or its transport number [3]:

$$n_1 = \frac{m_1}{K_1 I_t}, \qquad (2)$$

where $n_1$ is transport number of the i-th element, $m_1$ is the mass of the i-th element transported from one space to the other, I is the current in mA, t is the time in hours, and $K_1$ is the electrochemical equivalent of the i-th element. Calculated values for the zinc transport are shown in TABLE 2.

The data of TABLE 2 indicate that, within the region identified, the transport number is characterized by a constant value, 0.38, regardless of the level of current. In other words, 38% of the total current is used in the transport of zinc ions. The similar transport numbers for zinc in solutions of zinc nitrate and zinc sulfate are in agreement with tabulated data [4]. Within the region identified in TABLE 2, the transport number for zinc decreases approximately eight-fold and amounts to 0.05 on an average, i.e., all of 5% of the total current passing through the cell is involved in the transport of zinc. A decrease in the portion of current deployed in the transport of zinc should correspondingly lead to an increase in portion of current used for the transport of other ions. Under the conditions of the experiment, these ions would be nitrate or hydrogen ions.

TABLE 2. Transport Number for $Zn^{2+}$ at Various Concentrations of $HNO_3$ at the ER.

| Concentration of acid in ER, N | Current strength, mA | | | |
|---|---|---|---|---|
| | 10 | 30 | 100 | 300 |
| 0,01 | 1,40 | 0,41 | 0,43 | 0,40 |
| 0,1 | 0,37 | 0,41 | 0,36 | 0,38 |
| 0,3 | 0,08 | 0,17 | 0,37 | 0,34 |
| 1 | 0,03 | 0,05 | 0,06 | 0,33 |
| 3 | 0,04 | 0,02 | 0,04 | 0,04 |

Data on the accumulation of $NO3^-$ in the chamber simulating the external medium are presented in TABLE 3.

TABLE 3. Mass of Nitrate Ions transported to the External Medium.

| Concentration of acid in ER, N | $M_D$ mg | M,Mg | | | | $M_M$, mg | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Current strength, mA | | | | | | | |
| | | 10 | 30 | 100 | 300 | 10 | 30 | 100 | 300 |
| 0,01 | 2 | 18 | 40 | 95 | 310 | 16 | 38 | 93 | 308 |
| 0,1 | 15 | 26 | 48 | 128 | 330 | 11 | 33 | 113 | 315 |
| 0,3 | 44 | 50 | 100 | 130 | 350 | 6 | 56 | 96 | 306 |
| 1,0 | 170 | 180 | 195 | 320 | 650 | 10 | 25 | 150 | 480 |
| 3,0 | 670 | - | 710 | 800 | 1185 | - | 40 | 130 | 415 |

It is evident from the table that, in contrast to zinc ions, the quantity of nitrate ions being transported under the influence of the current shows little dependence upon the concentration of acid. It follows from this that nitrate ions do not participate in the redistribution of ions among their carriers.

The results of the determination of the quantity of hydrogen ions in the external medium are presented in TABLE 4.

TABLE 4. Quantity of Hydrogen Ions Transported to the External Medium.

| Concentration of acid, N | M, mg | | | | |
|---|---|---|---|---|---|
| | Current Strength, mA | | | | |
| | 3 | 10 | 30 | 100 | 300 |
| 0,01 | traces | | | | |
| 0,1 | 0,16 | 0,02 | traces | | |
| 0,3 | 1,05 | 0,8 | 0,45 | traces | |
| 1,0 | 3,9 | 3,3 | 3,3 | 1,3 | traces |
| 3,0 | 13,8 | 13,5 | 13,4 | 11,8 | 11 |

The data in the table characterizes the mass of hydrogen in the external medium associated with hydrogen diffusion from the ER. For its determination, the quantity of hydrogen ions formed during the anode process are subtracted from the total mass of hydrogen ions:

$$M = M_{\Sigma} - M_{A}, \qquad (3)$$

where $M_A$ is the mass of hydrogen ions formed at the anode (the value is determined by Faraday's Law), M is the mass of hydrogen ions associated with diffusion from the ER, and $M_{\Sigma}$ is the total quantity of hydrogen ions determined in the external medium.

In TABLE 4, one can clearly distinguish an area in which hydrogen is either not fixed at all or is found at the trace level. It coincides with the area identified in TABLE 2 for zinc, and it is characterized by its high transport numbers. Where the transport number for zinc is minimal, hydrogen ions are present in the external medium in elevated quantities.

The inverse dependence between zinc and hydrogen indicates that a redistribution of current in favor of hydrogen ions takes place at certain levels and concentrations of acid. On the other hand, when the transport numbers for zinc are high, hydrogen plays almost no role in the transfer of current across the membrane. Such conditions could arise when the migrational flux of ions proves to be equal to or greater than the absolute value of the diffusional flux and opposite in sign.

$$\frac{dM_M}{dt} \geqslant \frac{dM_D}{dt} \qquad (4)$$

Under these conditions, hydrogen ions cannot cross through the membrane to the external medium and the mass of the extracted element from the external medium is maximum.

The diffusion equation for thin membranes in the absence of a convective flow takes the form:

$$\frac{dM}{dt} = D_H S \frac{C_1 - C_2}{1}, \qquad (5)$$

where dM is the mass of hydrogen ions crossing through a membrane of thickness 1 and area S during a time dt, C1 and C2 are concentrations of hydrogen on different sides of the membrane, and $D_H$ is the diffusion coefficient for the hydrogen ions.

The velocity of migrational flux of hydrogen ions to the cathode side can be determined from the equation:

$$\frac{dM_H}{dt} = K_H I n_H, \qquad (6)$$

where dM is the mass of hydrogen ions crossing through the membrane to the ER during a time dt, I is the current strength, $K_H$ is the electrochemical equivalent of hydrogen, and $n_H$ is the transport number for hydrogen ions to a solution of nitric acid.

Substituting (5) and (6) into inequality (4), one can obtain the conditions for suppression of the diffusion of hydrogen ions from the ER as a result of electrical current by selecting the appropriate critical current $I_K$ :

$$I_K K_H n_H \geqslant D_H \frac{C_1 - C_2}{1} S \qquad (7)$$

or, taking into account that $j_K = \frac{I_K}{S}$,

$$j_K \geqslant \frac{D_H}{K_H n_H 1} (C_1 - C_2). \qquad (8)$$

By setting the coefficient $P=K_H \frac{D}{n_H l}$ and taking into account that a concentration of acid in the external medium did not exist prior to the beginning of the experiment ($C_2 = 0$), expression (8) can be represented in the form:

$$j_K \geqslant PC_1. \qquad (9)$$

The critical current density can be calculated if the diffusion coefficient of hydrogen ions is known for the medium being studied. The other parameters can either be determined from the conditions of the experiment ($c_{H+}$, S, 1) or found from tabulated data ($K_H$, $n_H$).

The diffusion coefficient of hydrogen can be determined experimentally for the cellulose and parchment membranes [1] used in the CHIM method. The experiments were carried out in an electrochemical cell. A diagram of the cell is shown in Fig. 1. It was found that the diffusion coefficient is independent of the concentration of acid in the ER, the composition and concentration of electrolyte outside the ER, and the area and thickness of the membrane. The average coefficient of diffusion equals $6,0 * 10^{-3}$ $cm^2/hr$ with a 12% margin of error.

Taking into account the value found for $D_H$, the coefficient of proportionality P in equation (6) can be quantitatively determined. The remaining parameters are: $K_H$- the electrochemical coefficient of hydrogen (0.00378 mg/mA); $n_H$ - the transport number for hydrogen ions in nitric acid, equalling 0.83 [3]; 1- the thickness of the ER membrane (cellulose and parchment membranes), equalling 8.10-3 cm. Then,

$$j_K \geqslant 25\ C_1 \qquad (10)$$

We attempted to use inequality (10) obtained for the simplest physico-chemical system, for complex systems and, in particular, for the extraction of elements associated with the use of the CHIM method in actual field conditions. The research was carried out in the Maritime Province (Far Eastern USSR) . At site 1[1], tin-rich ore stockwork occurs at a depth of 700 m hosted by interbedded sandstones and siltstones (Fig. 3). A tin ore body would not be noticeable on the basis of the results of a surface rock geochemical survey or trenching (see Fig. 3, graphs 1 and 2). It would not be determined by using the CHIM method if condition 10 (graph 4) were not fulfilled. If the required condition is fulfilled, on the other hand, the ore body would be discovered by CHIM survey (graph 5).

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[1] The Kavalerovo skarn type tin-polymetallic deposit

The small quantities of tin in mobile forms capable of moving under the influence of a current are so minuscule that the most favorable conditions would be necessary for the accumulation of tin in quantities sufficient for analysis. In accordance with inequality (8), such conditions can be realized in various ways. We used a change in $j_K$ at the expense of the membrane area. For this, CHIM method observations were conducted at three different element-receivers with membrane areas equalling 60, 7 and 1 $cm^2$ for current densities of 1.5, 20, and 150 $mA/cm^2$ respectively. The calculated critical current density ($j_K$) equalled 37.5 $mA/cm^2$.

CHIM observations were carried out along three parallel sampling lines at intervals of 1 m along profiles used for the surface lithochemical survey; the outcrops along the profiles were examined also. Fig. 3 shows that no tin anomaly appears in the case (graph 3) when $j < j_K$ ; extraction of tin amounts to 1-1.5 microgram. In the second case (graph 4) when $j < j_K$, a weak tin anomaly of up to 4 microgram against a background of 2 microgram is noticeable within a projection to the surface of the ore stockwork. However, the anomaly has poor contrast and is indistinctly delineated against the overall background. Finally, in the third variant of the survey (Graph 5), $j \ll j_K$ , a clear tin anomaly 250-m wide and coinciding with the projections to the surface of the ore body is obtained. Its intensity reaches 16 microgram against a background of 0.5-1.0 microgram.

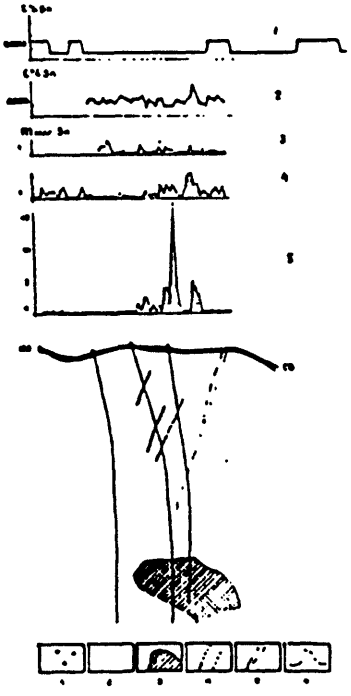

Fig. 3. Result of the CHIM survey at Site 1: 1) Quarternary deposits, 2) interbedded siltstones and sandstones, 3) tin-ore stockwork, 4) veins of tin mineralization, 5) veins of polymetallic mineralization.

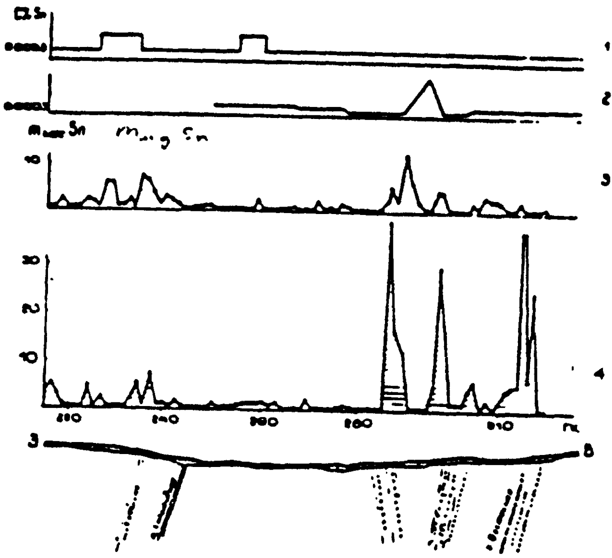

Fig. 4. Results of the CHIM survey at Site 11 (same legend as in Fig. 3).

Similar results were obtained at Site 11 (Fig. 4). the results of the soil survey and outcrops sampling are presented in graphs 1 and 2 respectively. The observations were carried out along two closely spaced lines: at one, the area of the ER was 7 $cm^2$ (Graph 3), at the other, the area was 1 $cm^2$ (Graph 4). Both in the first case ($j < jk$) and in the second ($j > jk$), two anomalous areas were noted on the profile: eastern and western. However, the intensity and contrast of the tin anomalies were significantly higher than when element-receivers with membrane areas of 1 $cm^2$ were used. The 1-$cm^2$ areas provided a current density for electrochemical extraction higher than the critical density; this was a higher current density than provided when using an element-receiver with a 7-$cm^2$ membrane. The 7-$cm^2$ membrane did not provide the required current density for the most favorable extraction of tin.

Investigation of the effect of the acid concentration in the ER upon the electrochemical extraction of metals characterizes one of the factors influencing the contrast and reproducibility of the results of observations using CHIM. Investigations of other factors will be discussed in subsequent reports.

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# THE MOVEMENT OF IONS IN ROCKS UNDER THE INFLUENCE OF AN ELECTRICAL CURRENT (Part II)

M. A. Alekseyeva

The features of ion movements within the liquid phase which we discussed in Part I were confirmed by subsequent study of moist rock environments. As a model in the investigation, we used quartz sand 0.14-0.25 mm in diameter. The sand was moistened by 0.0001-4 N. solutions of potassium chloride at moisture W from total moisture capacity W ~19% to W ~2.3%. The methodology of the investigations was the same as used in Part I.

The experiments were conducted in heat-proof cuvettes made from transparent organic glass. The cuvettes were 5-22 cm long, 2 cm wide and 2.5 cm tall. The prepared sand with a set moisture and KCl concentration was loaded in the cuvette. A direct electrical current was passed through the sand with the aid of platinum electrodes glued to the butt-ends of the curvette. The current density was maintained at constant $j = 0.5$ mA/cm$^2$ in all of the experiments. At a concentration of pore solution $C \geq$ In., the electric field strength E was measured on a V2-11 microvoltmeter. In the remaining cases, it was measured on a VK7-3 with input resistances of 300 and 1 MOhm respectively. The specific resistivity of the medium was $\rho = E/j$. In order to characterize the velocities of the ions $H_3O^+$ and $OH^-$, their movements l over a period of time t were measured. The mobility of the ions U was determined in terms of their velocities V $(V=l/t)$, $U = V/E$. The movement of $H_3O^+$ and $OH^-$ ions was recorded by the shift of the color boundaries from the electrodes (where the above mentioned ions are being recreated at a constant rate $j$ = const) to the center of the cuvette. In order to observe the shifts of $H_3O^+$ and $OH^-$ ions, a universal pH indicator was added to the electrolyte solution which moistened the sand. Created at the anode $H_3O^+$ ions, interacting with the indicator, colored the sand red, while $OH^-$ ions created at the cathode colored the sand violet and green. The positions of the color boundaries were noted at various times during the course of the experiment with the aid of scaled grid on the walls and lid of the cuvette. So that dilution of the pore solution at low moisture would not occur when the indicator was added, the indicator was first added to the sand in the quantity needed; then, after mixing and also during periodic remixings, the sand is dried in a thermostat at $t \leq 60°$ C. The required quantity of potassium chloride was added to the cooled sand. After a ten-minute remixing, the sand was loaded to the cuvette in small portions and tamped down. At the end of the experiment, several samples of sand were taken from the cuvette for a precise determination of the moisture at which the experiment was conducted. The difficulties associated with preparing a medium with a uniform moisture did not allow us to carry out experiments at moistures < 2%.

In a series of investigations, the rate of movement of the color boundary caused by differences in concentration of $H_3O^+$ and $OH^-$ ions on both sides of the boundary was measured immediately after the current was switched off: $V_M = l_M/t_M$, where $l_M$ is the length that the ions travel over a period of time $t_M$ from the moment the current is switched off, and $V_M$ is the rate of diffusion of $H_3O^+$ and $OH^-$ ions without current (this characterizes the component of their movement due to diffusion during passage of the current). Values for $V_M$ amount to several percent of the total rate of movement of ions in the case of 0.1 N KCl. These values did not exceed 20-30% at the highest concentration of KCl used, ~4n.

The processes taking place in the sand, both during the action of current and without current, are significantly more complex than in the case of a single liquid phase [1]. To the processes taking place in the solution itself, we must add the processes associated with the interaction of the solid and liquid phases. These processes lead to the formation of a double electrical layer at the phase boundary, a change in the overall given concentration of electrolyte and changes in concentration within pores at various distances from the solid phase, the solution of the solid phase under the influence of the current, the transformation of the double layers as a result of the solution process, the participation of the pH-indicator in their formation, etc.

As pointed out previously [1], the structure associated with ion movement when a single liquid phase is involved is different when the concentration of dissolved salt is more or less than 0.001 N. To be precise, at concentrations of KCl up to 0.001 N, the streams of $H_3O^+$ and $OH^-$ ions moving toward each other occupy the whole cross-section of the cuvette. At potassium chloride concentrations higher than 0.001 N, they separate into layers with the flow of $H_3O^+$ moving on top and the flow of hydrogen ions moving beneath, underneath the flow of $H_3O^+$. With a shift in the flow structure, the variation in their velocities change with increasing concentration of KCl, and at the same time the mobility of the $H_3O^+$ and $OH^-$ ions increases (Fig. 1). In the moist sand within the studied range of moisture between 2.3 - 19% at KCl concentrations of 0.0005-4 N., significant stratification was not observed. Nevertheless, variation in the velocities of the flows did occur, as did increases in the mobilities of the ions.

B-voltage

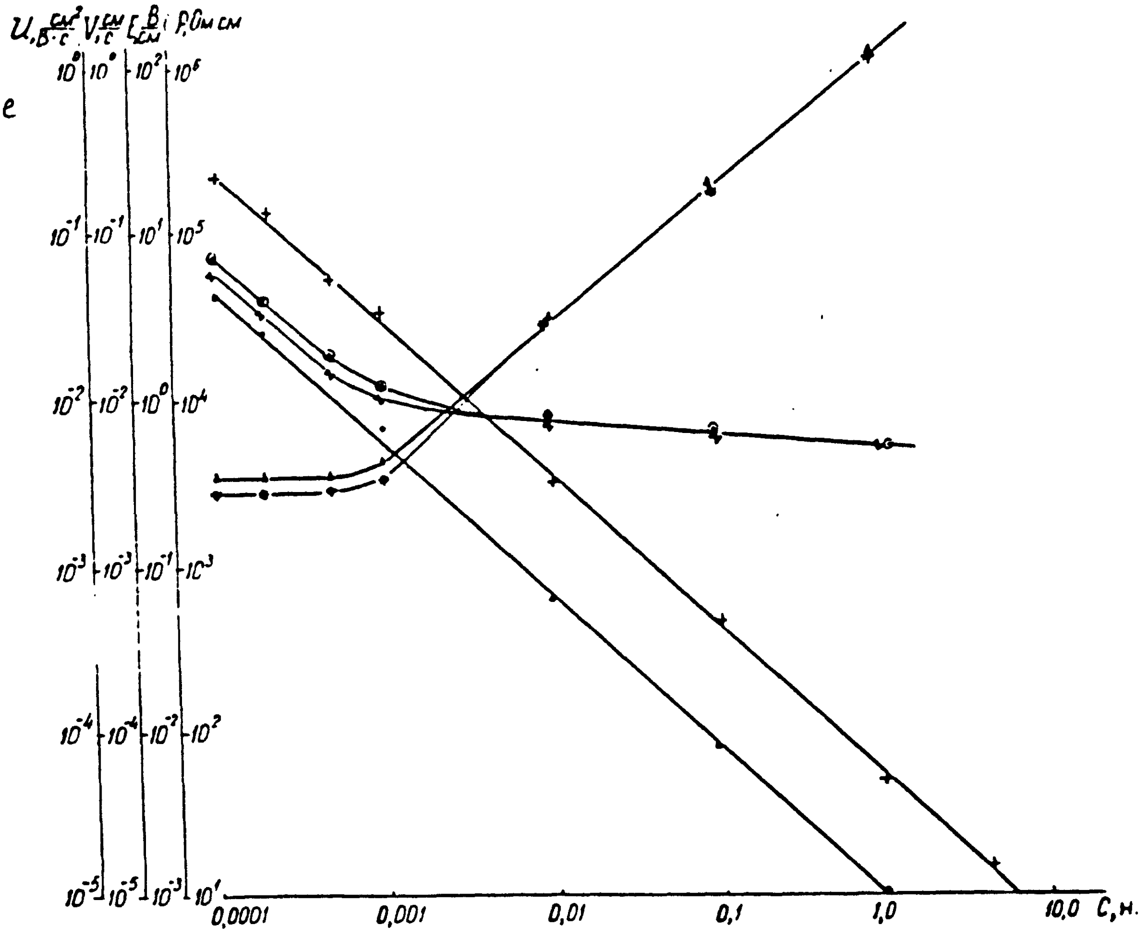

Fig. 1. Dependence of the solution resistivity ρ, electric field strength E, the velocity V, and the mobility of the ions U upon the concentration of KCl in the solution: x - E; • -ρ; ⊖ - $V^{H3O+}$; ⋈- $V^{CH-}$; ▲- $U^{H3O+}$; * - $U^{OH-}$.

As can be seen on figures 2, 3, and 4, the specific resistivity of the moist sand and the electric field strength fall with increasing concentrations of potassium chloride when the density of current passing through is held constant. The rate of movement of $H_3O^+$ and $OH^-$ ions decreases also. This decrease slows down when the concentration of KCl rises above 0.01-1.0 N. but the mobility of $H_3O^+$ and $OH^-$ increases. The increase in mobility is greatest at KCl concentrations greater than 0.1-1.0 N. For a sand moisture of 19% (Fig. 2), the relationships between decreasing specific resistivity and electric field strength and increasing concentrations of potassium chloride can be represented by straight lines on a bilogarithmic scale. Slopes of the lines coincide with those for a single liquid phase. Values of $\rho$ and E, however, are approximately 5 times higher in the sand than in the free KCl solution. The velocities of $H_3O^+$ and OH- ions, on the other hand, are lower in sand than in a unitary liquid phase. The decrease in the velocity during the transition from solution to sand varies at various concentrations of KCl, but exceeds an order of magnitude on an average. In the range of KCl concentrations from 0,0005-0.1 N, the velocity falls more sharply than within the range of KCl concentrations from 0.1-4.0 N. The change in the velocities of $H_3O^+$ and $OH^-$ ions within the range of low KCl concentrations occurs under a different slope. The curves of variation V on the one side and variation of $\rho$ and E on the other do not parallel one another as was observed in the unrestricted solution of potassium chloride.

In accordance with the change in the rates of movement of $H_3O^+$ and $OH^-$ ions, their mobility changes in an analogous fashion by an order of magnitude. The mobilities of these ions are an order of magnitude less in sand than in solution and increase most sharply with increases in the concentration of KCl beginning at 1 N. It is important to note that the mobilities of $H_3O^+$ and $OH^-$ ions at high KCl concentrations in sand exceed mobilities at low KCl concentrations in unrestricted solution.

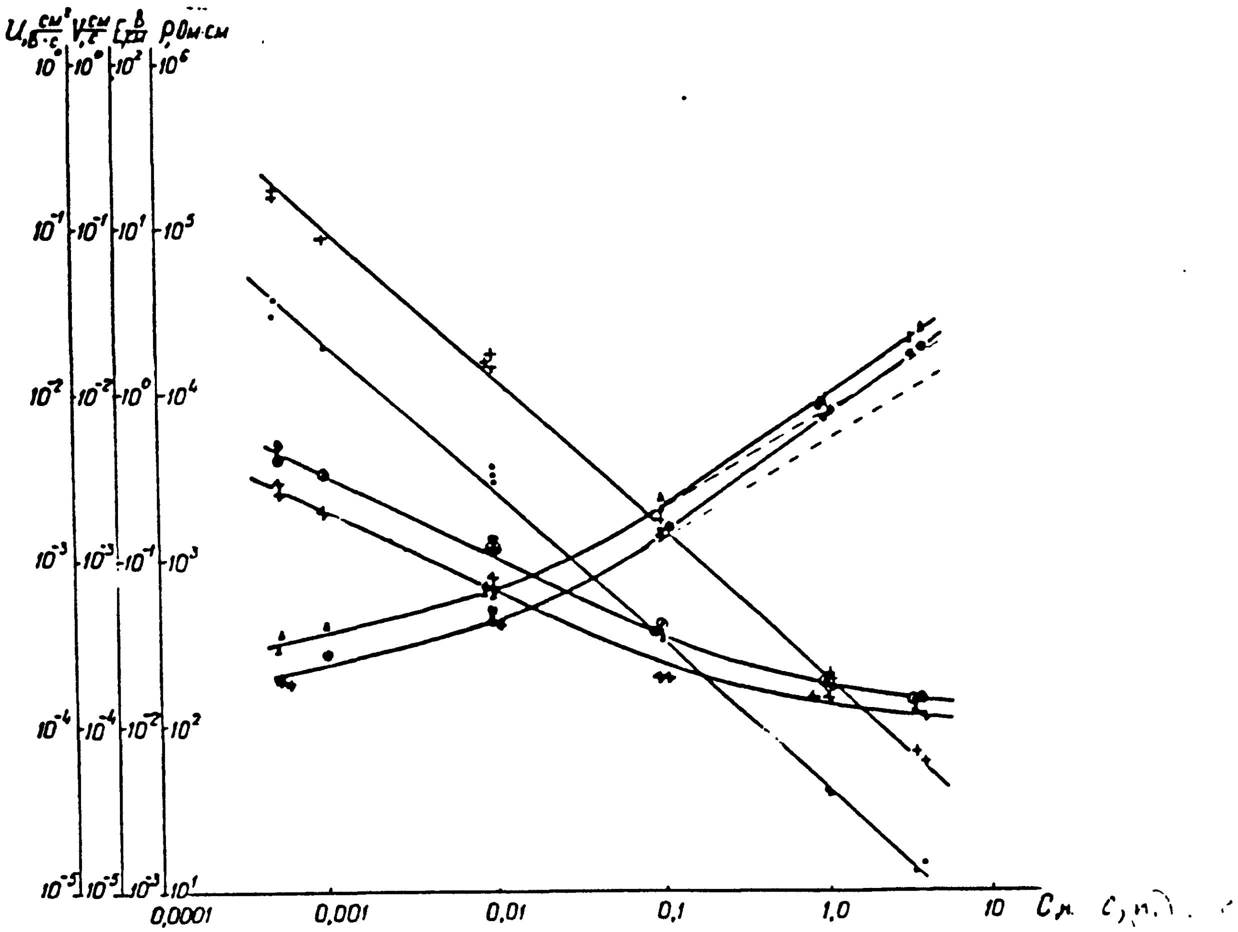

Fig. 2. Dependence of the specific resistivity $\rho$, the electric field strength E, the velocity V, and the mobility of the ions U upon the concentration of KCl - liquid phase at a sand moisture of 19.2%:

x - E; • - $\rho$; o - $V^{H_3O^+}$; ⊙ - $U^{H_3O^+}$; * - $U^{OH^-}$; U is calculated according to the formula $V-V_м/E$.

At a 4.5% sand moisture (Fig. 3), the specific resistivity and electric field strength increase more compare to $\rho$ and E in solution and sand under W = 19%. The increase of and E at W = 4.5% is ˜1.5 orders of magnitude greater in relation to that for sand at W = 19%. The curves of specific resistivity and electric field strength change in slope with changing concentrations of potassium chloride. The slopes become more gentle. The slopes of the curves for $\rho$ and E change positively. The dependencies discussed have a linear character only up to a KCl concentration C = 1 N. At higher concentrations of potassium chloride, the negative slope increases and becomes approximately the same as in the unrestricted solution and in sand with W = 19%.

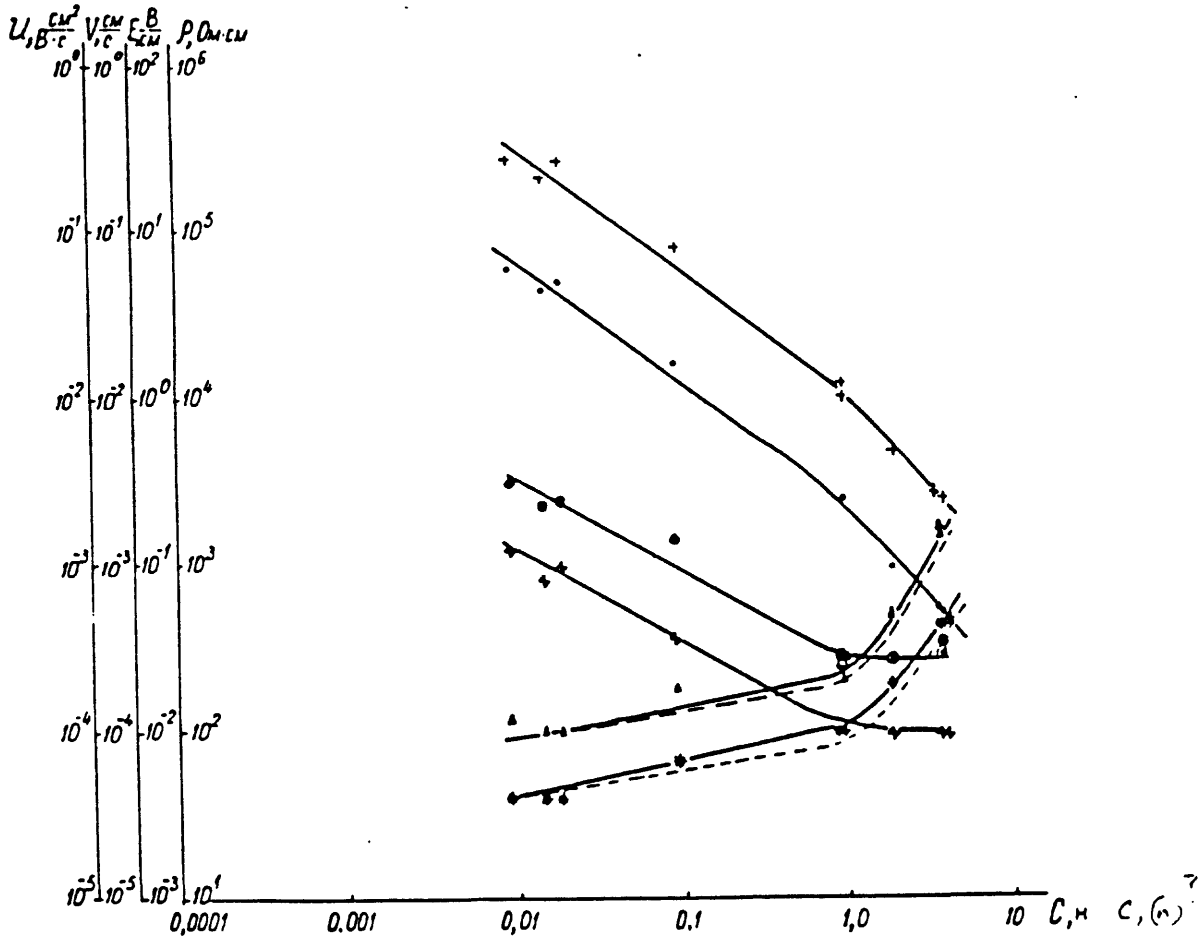

Fig. 3. Dependence of the specific resistivity of the solution, the electric field strength E, the velocity V, and the mobility of the ions U upon the concentration of KCl - liquid phase at a sand moisture of 4.5%: x - E; • - $\rho$ ; o - $V^{H_3O^+}$; ▬● - $V^{OH^-}$; ▲ - $U^{H_3O^+}$; * - $U^{OH^-}$; ----U is calculated according to the formula $V-V_M/E$.

In contrast to $\rho$ and E, the rate of movement of $H_3O^+$ and $OH^-$ ions does not decrease with decreasing sand moisture; it increases by a factor of approximately two. With increasing KCl concentrations (still less than 1 N), V, and E have similar slopes. The decrease in velocity slows abruptly at high concentrations. The mobility, on the other hand, generally increases with an increase in KCl concentration. The increase is most marked starting at C ~1 N. The mobilities in sand with W = 4.5% are 5-10 times lower than in sand with W = 19%. At C = 4 N, never the less, the mobility of $H_3O^+$ reaches a value similar to the value of U in dilute unrestricted solutions.

At a still lower sand moisture of 2.3% (Fig. 4), the specific resistivity and electric field strength become higher than at W = 4.5%. However, the increases in $\rho$ and E are insignificant, 1.5-2-fold. The dependences of $\rho$ and E upon C have a linear character in the 0.005-2 N range of KCl concentrations, and the slopes are more positive than at W = 4.5%. At KCl concentrations >2.0 N, the slopes of the dependences under discussion become more negative and approximate the slope values in an unrestricted solution and in sand with W = 19%.

The velocities of $H_3O^+$ and $OH^-$ ions at W = 2.5% practically coincide with those for sand at W = 4.5%. Until they flatten out, the slopes of the curves for V on a bilogarithmic scale are similar to the slopes of the curves for $\rho$ and E. The changes in the slopes occur at a KCl concentration of 2.0 N. The mobilities of the ions under investigation are 1.5-2 times less than the mobilities in sand with W = 4.5%. However, the values of U increase with increasing KCl concentrations and increase most sharply beginning at KCl concentrations of 2.0 N.

From a comparison of the results obtained, it is evident that the specific resistivity and electric field strength (at constant j) increase during the transition from unrestricted solution to moist sands. The velocities of the hydroxonium and hydroxyl ions drop sharply with the transition from solution to sands, but drop more or less identically at different moisture levels. At each value of moisture, the values of $\rho$ , E, and V decrease with increasing KCl concentration, but the mobilities of the $H_3O^+$ and $OH^-$ ions increase. Values of $\rho$ and E in unrestricted solution and in sand at W = 19 % decrease identically with increasing concentrations of potassium chloride, but the decreases in $\rho$ and E are different in regions of KCl concentration greater than or less than 1-2 N. At high concentrations, the degree of decrease of $\rho$ and E is the same as in unrestricted solution and in sand at W = 19%; while at low concentrations, the degree of decrease is less than in sands at W = 4.5% and 2.3%.

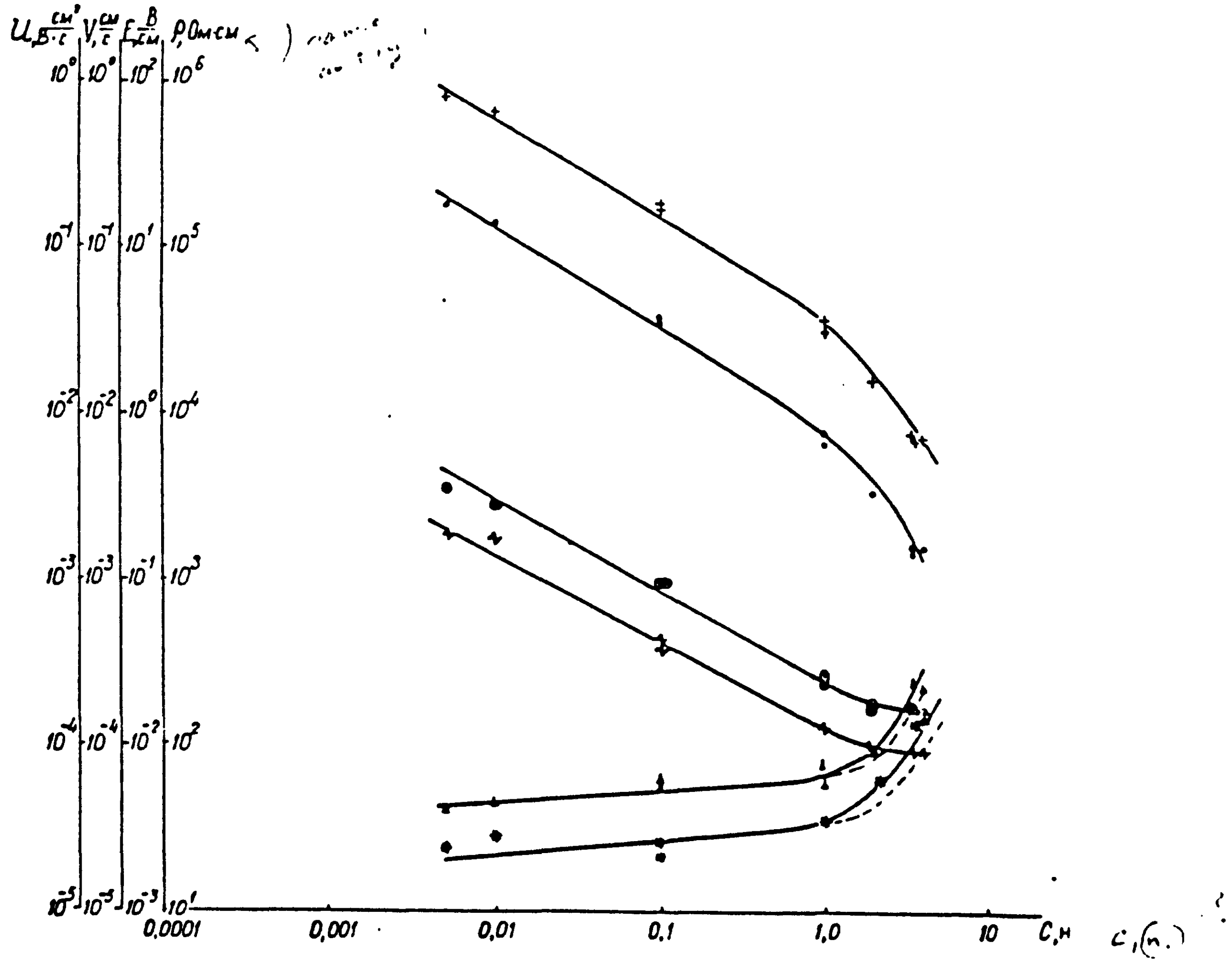

Fig. 4. Dependence of the specific resistivity of the solution $\rho$, the electric field strength E, velocity V, and mobility of ions U upon the concentration of KCl - liquid phase at a sand moisture of 2.3%: x - E; • - ; ⊙ - $V^{H3O+}$; ⋈ - $V^{OH-}$; ▲ - $U^{H3O+}$; * - $U^{)H-}$; ---- U is calculated according to the formula $V-V_{M}/E$.

In unrestricted solution and in moist sands, the decrease in the rate of movement of $H_3O^+$ and $OH^-$ as a function of C can be divided into two parts. At KCl concentrations $C < 0.1-2.0$ N, the degree of decrease is greater than at $C > 0.1-2.0$ N. Levels of concentrations at which there are changes associated with the decrease in rate of ion movement increase with decreasing moisture of the sand. In the part of low potassium chloride concentrations, it is also true that the degree of decrease of V with an increase of C in moist sands is less than in unrestricted solution and is independent of the amount of moisture. The degree og decrease in $\rho$ and E approaches this degree of decrease in sands with moistures of 4.5 and 2.3%. If the increase of $\rho$ and E at the transition from unrestricted solution to sands with total moisture content is correlated with, but not proportional to, the decrease in V, then there is no clear correlation between the increases of $\rho$ and E, on the one hand, and increases in the velocities of $H_3O^+$ and $OH^-$ on the other.

The mobilities of $H_3O^+$ and $OH^-$ ions differ, just as the velocities do, in areas of low and high KCl concentrations. The abrupt increase in mobility begins at higher KCl concentrations and lower sand moistures. The dependence of U upon C can be represented by the following empirical formulas:

| | in sands with low $C_{KCl}$: | in sands with high $C_{KCl}$: |
|---|---|---|
| W=19% | $U_{H_3O^+} = 18,8 * 10^{-4} * C^{0,24}$; | $U_{H_3O^+} = 75 * 10^{-4} * C^{0,6}$ |
| | $U_{OH^-} = 10,9 * 10^{-4} * C^{0,24}$; | $U_{OH^-} = 5,26 * 10^{-4} * C^{0,65}$ |
| W=4,5% | $U_{H_3O^+} = 2 * 10^{-4} * C^{0,17}$; | $U_{H_3O^+} = 1,43 * 10^{-4} * C^{1,56}$ |
| | $U_{OH^-} = 0,97 * 10^{-4} * C^{0,17}$; | $U_{OH^-} = 0,43 * 10^{-4} * C^{1,56}$ |
| W=2,3% | $U_{H^+} = 0,63 * 10^{-4} * C^{0,08}$; | $U_{H_3O^+} = 0,35 * 10^{-4} * C^{1,19}$ |
| | $U_{OH^-} = 0,36 * 10^{-4} * C^{0,08}$; | $U_{OH^-} = 0,24 * 10^{-4} * C^{1,29}$ |

Decrease in the mobilities of the hydroxonium and hydroxyl ions with decreasing sand moisture occurs to a less degree than the increase in $\rho$ and E and the decrease in V. For 0.1 N KCl, the dependence U-W was investigated in more detail for W = 2.3, 4.5, 8.5, 11.2, 14, and 19 weight-percent. On a bilogarithmic scale, the mobilities of the ions investigated form straight lines (Fig. 5) as a function of W and can be calculated according to the formula $U = KW^{\alpha}$.

The empirical formulas obtained have the form:

$U_{H_3O^+} = 1,1 * 10^{-5} * W^{1,8} cm^2/V*c$; $U_{OH^-} = 0,62*10^{-5}*W^{1,8} cm^2/V*c$

Taking into account the changes in velocity and mobility of $H_3O^+$ and $OH^-$ obtained, the specific resistivity and electric field strength at transitions from unrestricted solution to sands of various moistures and pore-solution concentrations, one can make several assumptions concerning the mechanisms of ion movement in porous media.

The sharp decrease in the velocities of $H_3O^+$ and $OH^-$ at the transition from unrestricted solution to moist sands when there are significant increases of $\rho$ and E indicates that an increase in the length of movement for ions in sands as compared to solutions has a substantial effect upon the mobilities and velocities of the ions. Since sands of the same fraction were used in the experiments, the increase in the length of travel at the transition from solutions to sands is greater than at a transition between sands of differing moisture. Probably, the rates of movement of ions in sands vary insignificantly with alterations in moisture and decrease sharply at the transition from solutions to sands. In addition, the specific resistivity increases with decreasing W, since not only the mobilities of the ions have effects on $\rho$ but also the masses of the ions, which decrease with lowering of the moisture.

In areas of low but increasing KCl concentrations, the change in the slopes of curves for $\rho$ and E on a bilogarithmic scale toward the decrease of negative slope and the change in the slope for the velocity of the ions, and also the approximation of the slope values at high KCl concentrations to its values in an unrestricted solution indicate the influence of an additional effect increasing the velocity and decreasing the specific resistivity. This is possibly a result of the influence of surface conductance. As is well known [3], the contribution of the surface conductance to the total conductance decreases with increasing concentration of pore solutions; this takes place at high C values. Thus, the rate of movement of ions in the areas of low concentrations of pore solutions is the sum of a component dependent upon the electric field strength and a component associated with the surface conductance.

For unrestricted solutions of KCl, it was demonstrated [1] that the motion of hydroxonium and hydroxyl ions in dilute solutions is primarily determined by the electric field strength and, at $C > 0.001$ N, by the hydrodynamic flows of the fluid caused by the electrochemical processes at the electrodes. The division associated with the changes in rate of movement of $H_3O^+$ and $OH^-$ ions as a function of KCl concentration into parts in the areas associated with high and low concentrations (a partitioning observed in unrestricted solution and in moist sands) indicates the possible role of a hydrodynamic factor. This factor is apparently also present in the porous media, exerting a more significant effect upon the motion of ions at high concentrations of the liquid phase.

, Besides the increases mentioned above, there are probably also increases in the intrinsic electrical mobilities of $H_3O^+$ and $OH^-$ ions with increasing concentrations of pore solution. For unrestricted solutions in the absence of convection, decreases in the mobilities of $H^+$, $Li^+$, $K^+$, $OH^-$, $Cl^-$ and other ions by ~20%

are noticeable as the concentration increases from 0.001 to 0.1 N. With further increases in concentration from 0.1 N to 1 N, increases in mobility by ~20% occur (5). For porous systems, some data have been presented concerning the increases of mobility of K⁺, Cu⁺, and other ions when the concentration of the liquid phase increases [2, 8, 9]. One should also note the reference of Malerbi [6] to Maneke and Bonkhover, who obtained an increase of electrical conductance in ion-exchange membranes at the transition from 0.1 N solutions of KCl to 1 N solutions. The majority of researchers believe that ions move in a double layer with velocities less or equal to those in an unrestricted solution [7]. However, the hypothesis has been put forward that mobilities of ions in a double layer could be greater than in the unrestricted portion of the pore solution because of the presence of a regulated structure associated with the solution [4]. In the opinion of the author, this is also possible.

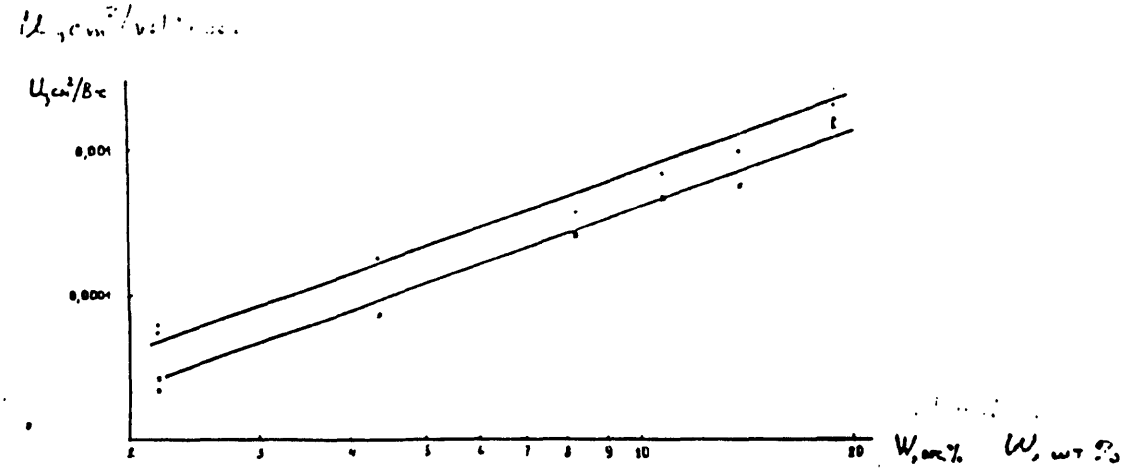

Fig. 5. Dependence of the mobility of ions U in sand with a 0.1 n. KCl solution upon moisture W: x - $U^{OH^-}$; • - $U^{H_3O^+}$.

The total mobility of ions recorded in the pore solution is a result of the simultaneous effect of many factors and several mechanisms. Practical application of the higher mobility of the ions requires the development of special instruments for differential recording of their movements and also further investigation of the mechanisms behind the transport of ions in porous media.

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# EXPERIENCE OF FINDING GOLD DEPOSITS IN WESTERN UZBEKISTAN USING THE CHIM METHOD

A. A. Veikher, A. A. Tazeev,
V. A. Gorbunov and A. I. Mernenko

Successful application of the CHIM method for discovery of covered polymetallic deposits in different regions of the USSR has led to the use of the method in exploration for gold deposits in Uzbekistan. The challenge to directly detect gold mineralization buried at appreciable depths increases in this region every year. The existing exploration methodology which consists of a combination of geophysical, geochemical, and geological methods and also drilling, becomes ever more expensive and labor-intensive with increasing depth of drilling. This expense is due to the following: 1) the need to replace surface soil sampling with deep lithogeochemical methods; 2) increased number of boreholes needed to be drilled to test geophysical anomalies verified by soil sampling and 3) use of in-hole geophysical methods at sites where surface methods are not capable of reaching the necessary depth. Under these conditions, it has become attractive to test the CHIM method since it allows to find covered ore deposits under unconsolidated alluvium more than 100-m thick during surface investigations.

It is difficult to use any new method. In addition, gold values in orebodies and geochemical anomalies are low in comparison to the contents of base metals in the same rocks. This requires special techniques for gold enrichment at the CHIM element-receivers and also the use of specific analytical methods for detecting the gold in the samples. All this is complicated by comparatively low sulfide content in the known gold deposits of Western Uzbekistan which are represented primarily by free gold disseminated in quartz-rich rocks. Such deposits provide very small quantities of gold in the mobile, water-soluble forms in which it can be leached by the CHIM method.

Another important feature for the field testing of the CHIM method in Uzbekistan is the abrupt change in moisture of the near-surface ground layer (it becomes very dry in the summer months) where the element-receivers (ERs) are set up. Fig. 1 shows that the specific resistivity of the soil from April to October in 1977 varied over an order of magnitude. This variation reflects the changes with respect to soil moisture and quantities of chemical elements in water-soluble forms in summer relative to the quantities of such elements in spring and fall. It is evident that these changes should be taken into consideration during the field work using the CHIM method.

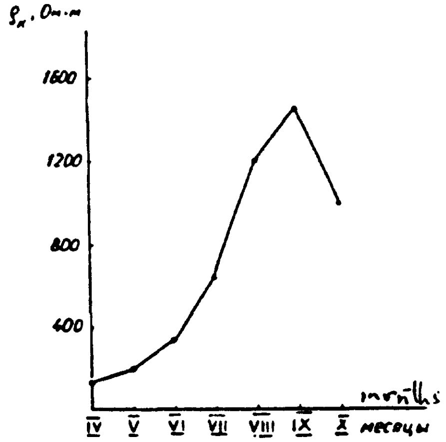

Fig. 1. Change in the specific resistivity of the soil with the seasons, 1977.

During the first stage of our CHIM survey, the possibilities for leaching gold in sufficient quantities for analysis were clarified and a correlation between zones of anomalously high gold leaching and known gold mineralizations. Operations were carried out at one of the known ore fields of Western Uzbekistan, where mineralization occurs at various depths,[1] including near the surface. Satisfactory leaching of gold was achieved under these most favorable conditions, and then the possibilities of its being leached under unconsolidated overburden several tens of meters thick were tested.

The gold deposit hosted by polymictic sandstones, siltstones, mudstones, phyllites and conglomerates folded into an anticlinal structure. The thickness of metamorphosed sedimentary sequence is 650-710 m. The deposit has been intruded by plutons of diabase and diorite composition. In general, the structure is a northwest-striking regional shear zone. On the intersection of the anticlinal structure and the shear zone, there occurs a zone of intensive silicification of sedimentary and magmatic rocks expressed as numerous veins, veinlets, silicified breccia, etc. The gold favors zones of silicification and is accompanied to some degree by sulfides.

The survey by the CHIM method was carried out at two areas. At the first, the ore body subcropped under 3-5-m thick overburden. The soil was represented by loam with a small humic upper horizon. Three profiles crossing the same elongated ore body but separated from one another by 100 m were selected for study. It was felt that three profiles were necessary in order to insure the reliability of the delineation of the gold vein. Each profile was sampled twice in order to characterize the reproducibility of the measurements. The second time, the profile was shifted 2-3 m to the side of the first, so that the ERs did not fall in the same holes, thereby excluding the possibility of contamination due to inaccurate testing associated with previous electrochemical leaching of gold.

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[1] "Well known gold deposit in Western Uzbekistan" is the Muruntau gold mine, biggest in the USSR (V.V. Strishkov, 1986; E.I. Bloomstein, 1987).

Taking into account our experience with the CHIM method in tracing gold veins at Rudnyi Altai Mountains, we used element-receivers with membrane areas of 40 $cm^2$ allowing leaching to be carried out in a high-power regime of current: 400-600 mA through each element-receiver. Other measures were employed to decrease the resistivity of the total power circuit. In particular, the auxillary power ground (anode) was flushed with 1.5-2 $m^3$ of water each day and carefully inspected for the presence of noticeably evaporating solution on the ER. In order to compensate for the evaporation on the ER, a portion of the solution was added periodically (after 5 hours). The shallow holes where the ERs were set up were carefully loosened and moistened with distilled water.

Investigations using the CHIM method were carried out at the first area in the middle of June. During the first days of the survey, the temperature was 25-30°C. The temperature then increased regularly; the original specific resistivity of the soil at 100-200 Ohm increased to hundreds and thousands of Ohm.

The results of the observations of gold-leaching during the first 10 hours and the next 10-20 hours along the first of the profiles (Fig. 2) indicate that the gold vein and the country rock adjacent to it could be satisfactorily delineated by anomalies of 0.03-0.04 mcg of leached gold relative to a background of 0.01 mcg during both tests. The leaching of gold differed at individual points, but anomalies generally coincided in space. The same situation was observed along other profiles. Graphs of CHIM constructed on the basis of the data of the first test are presented below.

Sampling repeated along a profile with an offset of 5 m from the first are shown in Fig. 3. From Fig. 3, it is evident that anomaly above the ore body was detected here at the same intensity of 0.035 mcg against a background of 0.01 mcg.

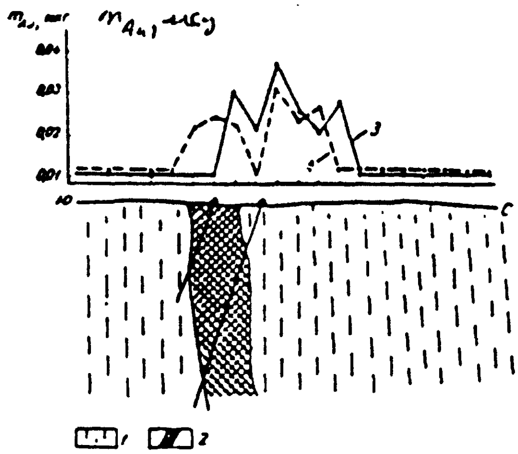

Fig. 2. Results of observations using the CHIM method at area 1. Profile 1: 1) host rocks, 2) ore body, 3) curves of gold-leaching for the time 0-10 h (3) and 10-20 h (4).

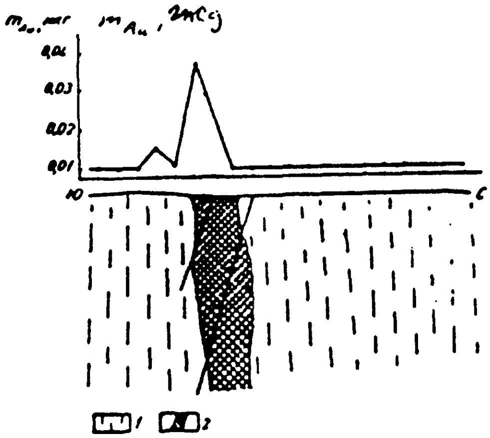

Fig. 3. Results of observations using the CHIM method at Area 1. Observations repeated along a profile offset from Profile 1 by 5 m: 1) host rocks, 2) ore body.

However, the anomaly became noticeably narrower and conformed more strictly to the gold vein itself.

The cause of the changes in the width and structure of the anomaly on the profile repeated with a 5-m offset is not clear. It is important to mention that it was precisely at this time that an intense increase in temperature and a change from spring humidity to summer dryness took place. The first profile was

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sampled in the late spring when the summer had just begun. The second profile was sampled when the hot summer had arrived. It is possible that it were these circumstances which brought about the change in the dimensions of the anomaly. Other causes are possible. Unfortunately, a profile was not completed during the third phase, the period of complete dryness. The need for such observations became apparent later, after measurements were carried out along other profiles and in other areas.

A second profile offset from the first by 80 m was sampled at a still drier time than Profile 1. Fig. 4 shows that the orebody was satisfactorily identified by gold CHIM anomaly. Its character is similar to that observed on the parallel Profile 1. Repeated observations along profiles 2 and 2', separated from one another by approximately 3 m, yielded the same correlation. However, it is necessary to note that the intensities of the anomaly and background decreased for Profile 2 in comparison to Profile 1, becoming 0.01-0.15 mcg and 0.0025 mcg respectively. In other words, the quantity of leached gold decreased by a factor of approximately 3-4 in more or less identical fashion both in the anomaly and in the background. The latter decrease, by the way, requires special investigation.

The decreases in the intensities of the anomaly and the background during the leaching of gold along Profile 2 relative to intensities along Profile 1 indicate that the cause is of a general character: a significant decrease in humidity. Features of the leaching due to changes in the gold content within the mineralization, for example, did not have a significant effect upon the change in the intensity of leaching, since they affected the anomaly and the background to more of less equal degrees.

On Profile 3, 100 m to the west of Profile 2, the gold-leaching anomaly presented in Fig. 5 has a lesser intensity than the ones along profiles 1 and 2. Moreover, the intensity of gold-leaching in areas of the profile with host rock remained the same as for Profile 2. This demonstrates that there are differences in the ore-grade and style of the mineralization and between these two profiles, and they caused the decrease in the intensity of the anomaly. Actually, Profile 3 was located at the marginal portion of the vein, where the gold content is less than in the vein's central portion and where the thickness of the cover is somewhat greater than over profiles 1 and 2, reaching 6-7 m, and, locally, 10 m.

Evaluating the results of the CHIM method at the first area, one can see that an ore body in the form of a quartz-gold vein can be satisfactorily delineated by the new method when using a high-power regime for leaching the gold (400-600 mA for an ER membrane area equalling 40 $cm^2$). Climatic conditions lowering the quantity of gold leached during times of dryness had a substantial effect upon the CHIM results. For CHIM anomalies to be noticeable, it is necessary to leach the gold at high values of the current strength. The effect of the climatic conditions can be evaluated by their simultaneous effect upon the intensity of the anomaly and the background. The fact that the changes along the profiles are not identical indicates variations in geological styles of the mineralization and its bedding.

Further surveys using the CHIM method were carried out under conditions of low soil moisture in the area of unconsolidated alluvium several tens of meters thick at Area 2, which is underlain by sedimentary and volcanic sequences of the Lower Paleozoic age. Intrusive rocks, represented by granosyenites, syenites, granites, and syenite-diorites, are common in the area. Uuconcolidated deposits of Neogene-Quarternary age in the form of loesses and loess-like loams lie on an eroded surface of Paleozic rocks or on Lower Quarternary conglomerates. The thickness of the unconsolidated deposits varies from 0.3 to 40 m or more. The gold mineralization is primarily controlled by a system of faults with steep north-east dips (100-110°). The ore bodies are represented by quartz veins, stockwork, and fractured zones. The thicknesses of the veins vary from 0 to 2.5 m. These small thicknesses do not prevent from being traced for more than 2000 m. The veins are displaced faults of a strike-slip character. Gold with the veins is present in the native form as electrum. Together with the gold in the veins, silver occurs bonded with sulfides, pyrite, and arsenopyrite. The quantity of the latter does not exceed one percent. In addition to silver, Hg, Bi, Cu, Sb, and a number of other elements are present in the form of admixtures. From among other ore minerals, there are small quantities of sphalerite, galena, chalcopyrite, molybdenite, pyrrhotine, etc.

The operations at the Area 2 were conducted during a period of extremely low soil moisture following a long period of dryness and also under conditions of intense evaporation of solutions from the element-receivers. In order to provide a strong current for the leaching of gold, measures were taken to reduce the total resistivity of the power circuit in addition to the steps described above. A set-up of element-receivers with "channels" was included in the new measures used. The essence of the method consisted of digging a hole 30x30 cm and 10-15 cm deep and then poking a crow-bar through the center of the hole to create a channel 3-5 cm in diameter and 50-cm deep in the center of the hole. One then pours 200 ml of distilled water into the channel formed and covers it with pulverized and screened soil to the point of creating a liquid slurry both in the channel itself and in the center of the hole. The ERs are set up in this mixture. A large area of contact between a moist layer and the surrounding soil is thus created and an horizon with higher moisture is also reached. The other measure taken consisted of carrying out the leaching primarily at night in order to decrease the evaporation of the electrolyte from the element-receivers. The results of the CHIM method application on the first of the profiles (Site 2) is shown in Fig. 6. The thickness of the overburden of unconsolidated sediments amounts to approximately 20 m here. The results are presented in the form of two measurements along the first profile and along a profile parallel to the first but off-set by 3 m. The figure shows that the ore body makes a sharp, contrasting anomaly of up to 0.04-0.06 mcg for a background of 0.005 mcg. The background was characterized by a single point in connection with the small thickness (approximately 2 m) of the quartz-gold vein (the spacing of observations was 10 m) but reproduced well during repeated samplings. In this case, the anomaly delineated for a thickness of unconsolidated deposits equalling approximately 20 m is similar to that delineated when the thickness of such deposits was several meters (Site 1).

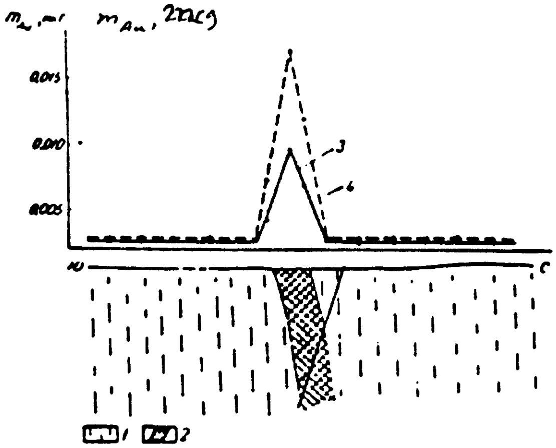

Fig. 4. CHIM results at Area 1. Profile 2: 1) host rocks, 2) ore body, 3) curve of gold extraction along the primary profile 2, 4) curve of gold extraction along the parallel profile offset from the primary one by 3 m.

Several hundreds of meters from that profile, CHIM testing was carried out along still another profile where the total depth of occurrence of the gold-quartz vein was approximately 40 m. The deposit at this location was hidden under conglomerates 10-20 m thick and loesses of the same thickness. The results of the tests, shown in Fig. 7, reflect a satisfactorily delineation of the gold vein under these conditions.

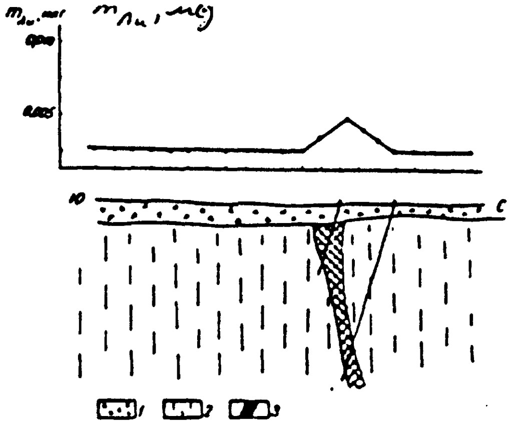

Fig. 5. CHIM results at Area 1. Profile 3: 1) alluvium, 2) host rocks, 3) ore body.

Thus, electrochemical leaching of gold using the CHIM method allows the discovering of gold objects covered by unconsolidated rocks tens of meters thick. Apparently, an approximately 40-m depth of occurrence of gold veins does not constitute a limiting depth for this method. Thus far, however, no veins have been found at greater depths. It is necessary to note that the thickness of the vein does not have a significant effect upon the detection of anomalies. Veins with thicknesses of either 2 or 10 m can be delineated during surface observations using the CHIM method.

The results of testing the CHIM method for discovery of gold mineralization covered by unconsolidated rocks in Western Uzbekistan, in principle, demonstrated a possibility for the use of this method. During the course of testing, several techniques were developed for conditions involving low or sharply varying soil moisture. The experience gained facilitated projects dealing with sorting of anomalies of electrical conductivity and consequent polarization which resulted in differentiation of areas containing gold from pyritized zones or other non-gold-bearing zones.

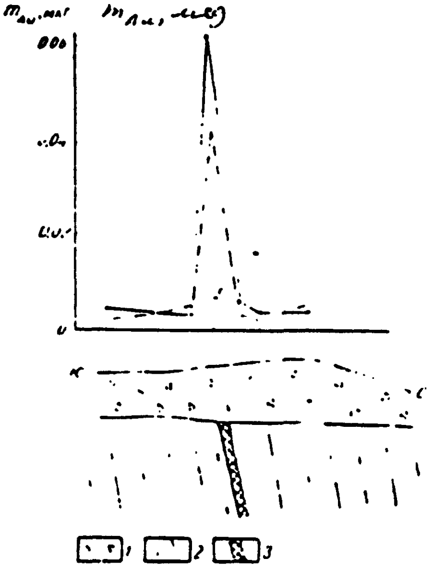

Fig. 6. Results of observations using the CHIM method at Site 2. Profile 1: 1) loesses, 2) host rocks; curves of gold-leaching on the first (4) and the parallel profile offset from the first by 3 m (5).

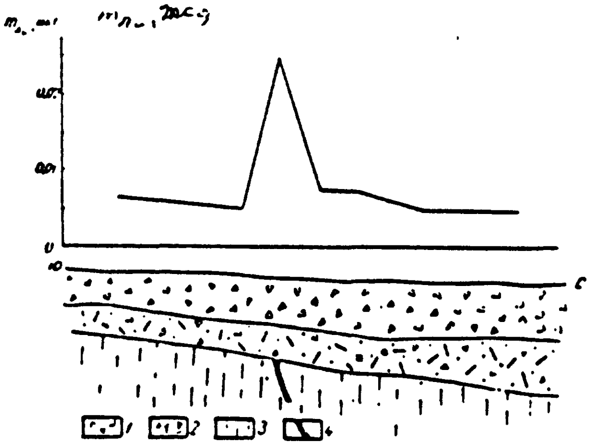

Fig. 7. Results of observations using the CHIM method at Site 2. Profile 2: 1) loesses, 2) conglomerates, 3) host rocks, 4) ore body.

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# POSSIBLE USES OF THE CHIM METHOD FOR EXPLORATIONS OF COVERED GOLD DEPOSITS

S.G. Alekseyev, A.A. Veikher and I.S. Goldberg

A successful application of the aureole version of CHIM method in exploration for covered copper, polymetallic and nickel deposits located with unconsolidated overburden reaching 100-m in thickness suggests that this method could be used in search for gold deposits as well. The main difficulty with gold deposits using the CHIM method is the fact that gold content in the ore bodies and surrounding aureoles is low (four-five orders of magnitude lower than copper, nickel, lead, zinc, and a number of other metals). Overcoming this difficulty would be possible by increasing the sensitivity of gold analysis in samples from element-receivers and increasing the enrichment of samples during the process of electrochemical extraction. We undertook efforts in both directions. The results of our investigation are described below.

In order to increase the sensitivity of the gold analysis in the CHIM samples, we used a method of film polarography with accumulation on a solid graphite electrode. The ethyl ether of acetic acid (ethyl acetate) was used as the extracting agent. Extraction was carried out for 2 minutes on samples 10-ml in volume with the aid of 10 ml of ethyl acetate. Determination of the gold using film polarography with accumulation allowed us to concentrate the microquantities of gold at the graphite electrode's surface. This increased the sensitivity of the determination by a factor of 10-20. The use of a solid graphite electrode significantly simplified the technique of analysis over what was possible with the use of mercury electrodes. At the same time, we used a polarograph FPL-1 which was specially developed for field laboratories. The use of this polarograph may have also increased the sensitivity and productivity of analysis for each sample.

These measures allowed us to achieve a sensitivity of gold determination equal to 0.005 mcg/ml in the solution analyzed or a sensitivity of 0.01 mcg for the entire volume of the sample. The error of the determination was 30%. The gold analysis of CHIM samples for gold involved the following steps:

- The sample solution was evaporated to a volume of 10 ml and transferred to a separatory funnel;

- 5 ml of concentrated hydrochloric acid and 10 ml of ethyl acetate were added to this volume. Distilled water was then added up to a volume of 30 ml;

-extraction was carried out for two minutes;

- the aqueous phase was decanted, and the ethyl acetate was washed with 0.1 N hydrochloric acid;

- ethyl acetate was transferred to a heat-resistant 50-ml beaker; 2-3 drops of a 2% solution of NaCl were added and the mixture was evaporated to dryness in a water bath;

- the dry residue was dissolved in 0.5 ml of aqua regia, 3 drops of hydrogen peroxide were added, and the mixture was evaporated to moist salts;

- the moist salts were treated with 0.5 ml of concentrated hydrochloric acid and evaporated to a dry residue;

- the dry residue was dissolved in 2 ml of 0.1 N hydrochloric acid and transferred to a cell for polarography on the FPL-1;

- polarographic analysis of the solution was carried out in the regime: sedimentation (settling potential) - 0,7 V; sedimentation (settling) time - 10 min; scanning rate - 1.6 V/min; range of current recording - 2 mcA;

- a polarographic curve of gold-solution currents was recorded and the height of the maximum on the curve was measured;

- the concentration of gold in the analytical solution (2 ml) was determined according to a calibration graph;

- the mass of gold in the sample was calculated on the basis of the volume taken for the analysis of the sample.

A more detailed analytical methodology would require a special publication and is not discussed in the present article.

Using the analytical methodology just described, measures were taken to increase the concentration of gold in the samples during the process of electrochemical extraction. The investigation was conducted on one of the gold deposits where the gold mineralization is associated with a series of faults concordant with the bedding of host rock. The mineralization was covered by unconsolidated overburden up to 40-m thick.

During the first stage of the investigation, attempts were made to confirm the fact that gold is indeed extracted from soils when using the CHIM method. For this purpose, we selected a pediment area where the presence of gold was established in trench samples. For the electrochemical extraction, we used equipment normally used for CHIM surveys of copper, zinc and lead deposits. The experimental regimes were set up to clarify the gold extraction for various time periods, various strengths of electrical current, and , correspondingly, for various electric field strengths around the element-receivers. In addition, the gold extraction in the form of cations or anions was investigated by connecting element-receivers to a negative or positive pole of current source at the CHIM-10 station.

The results of the observations show that traces of gold could be found at sites where mineralized rocks outcrop directly under slope deposits only when using enhanced extraction regimes (a higher electric-field strength of ~1.0 V/cm and appreciable current - up to 400 mA). We were not able to determine gold at other current levels. Extraction of gold took place in cationic and anionic forms in approximately equal quantities.

The observations showed that increases in the level of current through the element-receivers caused increases in the quantities of gold accumulated. This led us to a conclusion that it might be possible to move from qualitative recording of traces of gold to actually measuring its amount by increasing the level of current (and, correspondingly, the electric-field strength).

When attempting to increase the current, however, it turned out that the standard element-receivers (in which the parchment membranes in contact with the soil have an area of 5 $cm^2$) heated up, and the membranes burned. Therefore, the element-receivers used would not allow passage of a current larger than 300-400 mA for the time period necessary (10-20 hours).

In order to raise the current through the element-receivers and avoid having the element-receivers heat up, it was necessary to lower ground resistance of the element-receivers. The latter goal was achieved by increasing the area of the membrane in contact with the soil. Element-receivers with membrane surfaces of 15, 40 and 300 $cm^2$ were tested. The current through the element-receivers was correspondingly increased to 400-600 mA under comparable conditions, and the masses of extracted gold increased to 0.015, 0.1, and 1.0 mcg respectively.

It follows from the data presented that one can anticipate extraction of measurable quantities of gold exceeding the reached limit of sensitivity for the analytical determination of gold (0.01 mcg) when using membrane-surface areas of 40 $cm^2$ or more. Using these element-receivers at a current of ~400 mA, we attempted to distinguish gold mineralization not only in shallow pediment conditions but also present at depth under clay-rich overburden with thicknesses of 10-20 and 40 m.

The results of initial and repeat observations during 1976 on one of the profiles where the thickness of unconsolidated overburden reached 20 m indicate (Fig.1) that two ore zones crossed by the profile are satisfactorily identified by anomalously high extraction of gold (see Curve 1). The repeat observations (Curve 2) coincide well with the initial ones. Some shift in the location of the anomalous samples is due to the non-uniform distribution of gold in soil and to the fact that the repeated observations were carried out along a profile offset from the first one by 2 m.

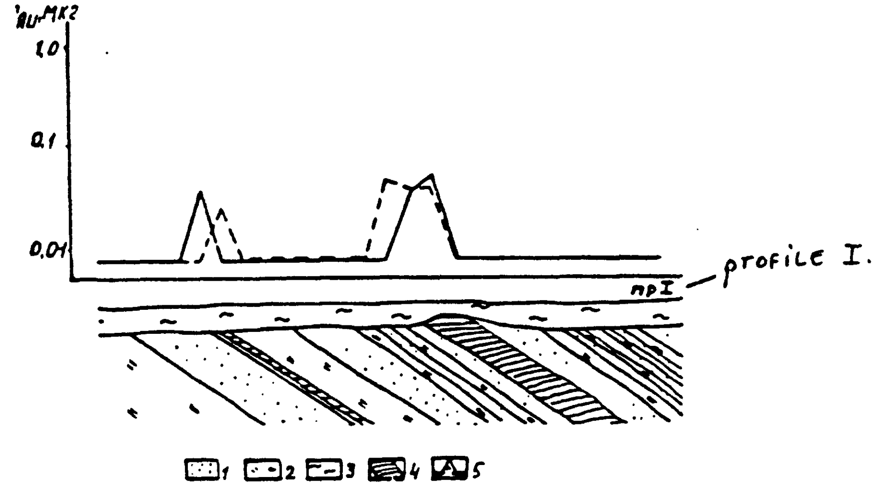

Fig. 1. Results of the CHIM survey. 1) sandstones, 2) siltstones, 3) clays, 4) zones of gold mineralization (gold content > 0.01 ppm), 5) curves of gold extraction.

In order to confirm the reliability of the results, the repeat sampling was conducted along a profile offset from the first one by 40 m along the strike of the ore zone. The repeat data (Fig. 2) show good correlation of zones of gold mineralization along strike.

In one year, control tests were made as to how reproducible the extraction of gold would be with changes in climatic factors and other environmental factors which are difficult to take into account. Measurements were made during a more humid and colder period of time than during the preceding year. In such circumstances, one would anticipate a change in the equilibrium between mobile and fixed forms of gold toward a decrease in the quantity of gold in mobile forms. The results of the measurements indicate that, in fact, extraction of gold was achieved only in isolated sample points in the anomalous zones and, second, there was an overall decrease in the amount of leached gold. Thus it became evident that the amount of leached gold necessary for satisfactory delineation of gold mineralization has to be increased to a higher level which would certainly exceed the climatic fluctuation in the mass of extracted gold. In fact, this makes one question the use of element-receivers with large membranes in the CHIM methodology.

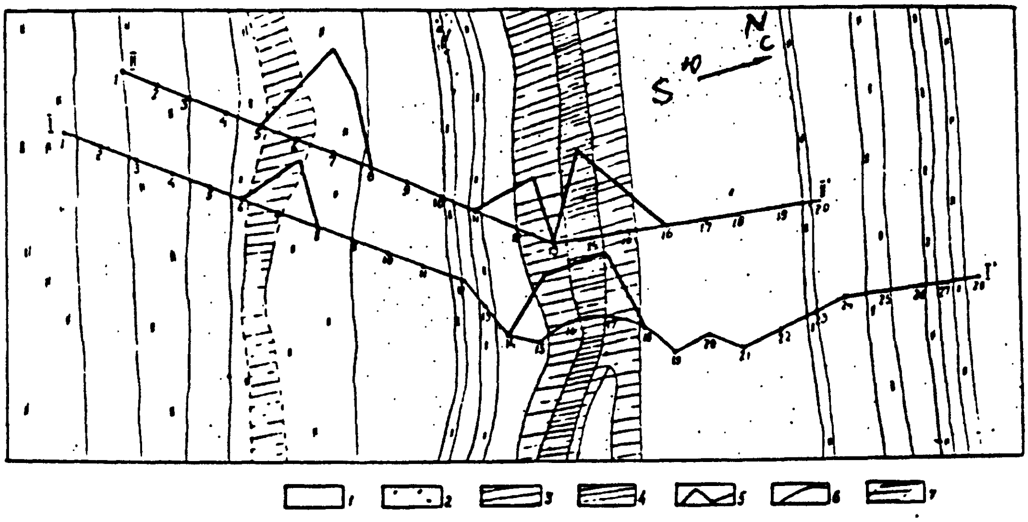

Fig. 2. Geological sketch of the CHIM surveyed area. 1) sandstones, 2) siltstones, 3) zone of gold mineralization (gold content 0.1-0.3 ppm, 4) ore bodies (gold content > 3.1 ppm, 5) gold-extraction curves, 6) sample profiles, 7) zones of gold mineralization suggested by the CHIM method.

The use of element-receivers with membrane surfaces of more than 100 cm$^2$ is associated with a number of difficulties: passage of the electrolyte, the complexity of construction, inconveniences with respect to transportation, etc. In order to increase the mass of gold leached, it is expedient to group together several element-receivers with a large membrane. The sample results along Profile I are shown in Fig. 3 for a grouping of four element-receivers with membrane areas of 40 cm$^2$ in the same area where in 1977 the gold extraction from one element-receiver was on the detection limit. A comparison of the data shows that the grouping of four element-receivers provides a satisfactory delineation of gold mineralization. The analytical data and quantities of extracted gold were reproducible.

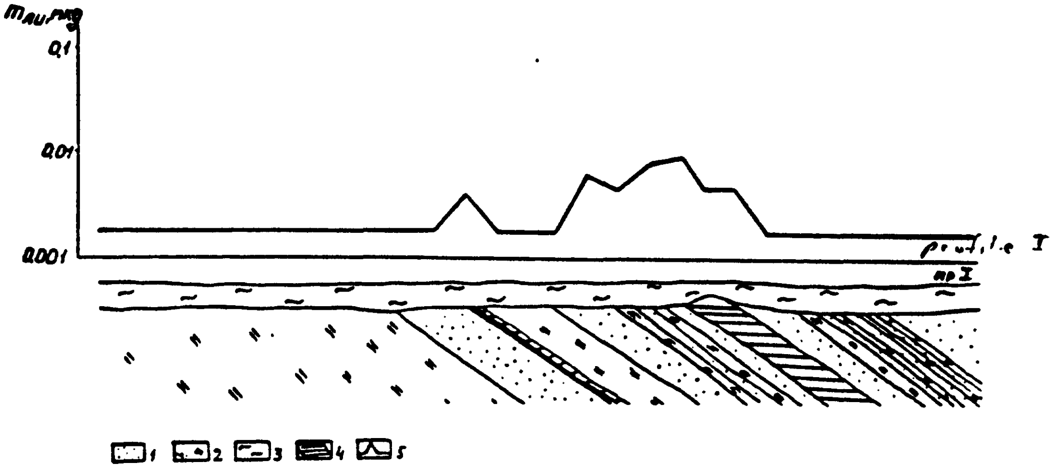

Fig. 3. The CHIM results based on combining of solutions from several element-receivers (for legend, see Fig. 1).

Thus the investigation lead to the following conclusions:

1. The CHIM method in the aureole version can be used to delineate gold mineralization under an unconsolidated cover, just as it can be used to delineate copper, lead, zinc, and other metals.

2. For successful determination of gold mineralization, it is necessary to use a high-power extraction regime (~0.5 A per element-receiver). This can be facilitated by enlarging membrane areas for the element-receivers and by grouping element-receivers together.

For the area of CHIM survey, the combining of solutions from 3-5 element-receivers with membrane areas of 40 $cm^2$ facilitated satisfactory delineation of gold mineralization under various climatic and environmental conditions. However, it is necessary to conduct an orientation survey for the selection of an extraction regime in each new area.

## Additional case history.

The CHIM survey to trace gold mineralization covered by unconsolidated overburden (Fig. 4) was conducted in the test area using the extraction conditions described above. At sites where the cover was not thick, the gold mineralization was outlined by trenching and pitting.

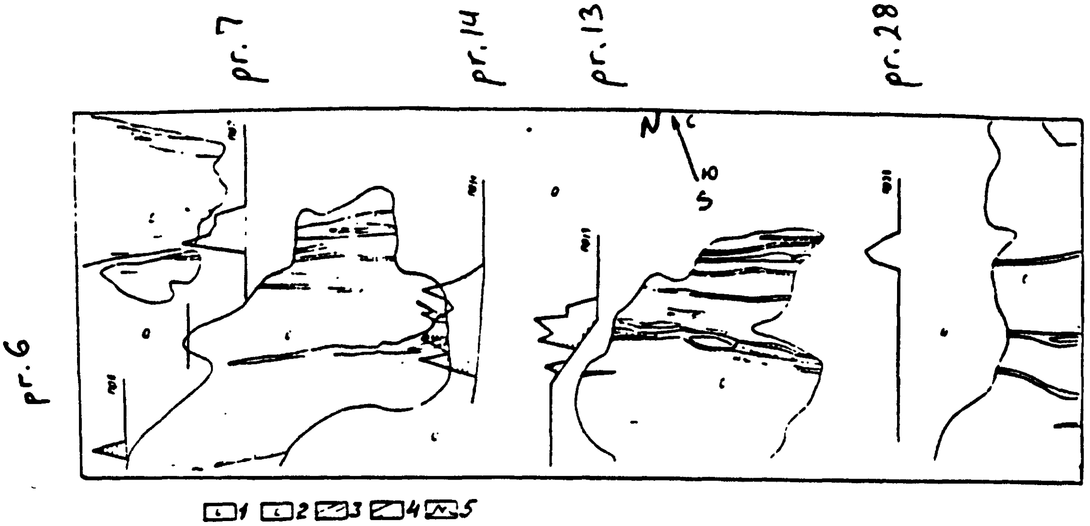

Fig. 4. Geological sketch of the CHIM survey area. 1) Quarternary alluvium, 2) Early Carboniferous sedimentary formation, 3) zones of gold mineralization (gold content 0.1-3.0 ppm), 4) ore bodies with gold contents > 3.2 ppm, 5) gold-extraction curves.

It is evident from Fig. 4 that high grade mineralization occurs in the central portion of the area. Two ore zones covered by unconsolidated overburden can be delineated here. The northern zone probably extends beyond Profile 14 to Profile 7, gradually becoming too low-grade in a northwestern direction. Low grade is also noticeable within this zone in the opposite direction, beyond Profile 28. The southern zone has a limited high-grade area. Its distribution to the northwest and southeast was not known before the start of the CHIM survey.

The results of the CHIM survey along Profile 14 and 18 allow us to confidently outline the southern zone in covered area between two outcrops in the central part of the area. A continuation of this zone was not found on profiles 28 and 6. Thus the ore zone established at the outcrop can be satisfactorily traced under alluvium and can be contoured from the northwest and southeast. The northern zone was not found on profiles 18 and 14, but is well delineated on profiles 28 and 7. From what has been said, we can conclude that this zone has a high-grade portion in the vicinity of Profile 18 and that the zone outcrops at the surface to the northwest. Further to the northwest, the zone becomes low-grade, but it again becomes high-grade near the Profile 7. The high-grade portion of the zone is limited in extent along strike. Such limitation was also noted in the area of Profile 28.

Besides the northern and southern zones traced by the CHIM method, high quantities of gold probably outlining still another gold-zone extending further to the northwest were extracted on Profile 6.

The results obtained by the CHIM method serve as a basis for drilling priorities in the southern zone.

The survey results within this area showed promising possibilities for using the CHIM method to trace gold mineralization beneath the unconsolidated cover. However, the methodology of field operations using the CHIM method in exploring for gold under various geologic, geomorphologic, and climatic conditions requires further development. Nevertheless, the very fact that deep-covered high-grade gold mineralization can be delineated is significant and allows us to consider the CHIM method for the prospecting of vast covered areas and for evaluation of gold prospects already discovered.

# EXPERIENCE OF ANALYSIS OF CHIM SAMPLES FOR GOLD

G. P. Fedorova, G. F. Vasilkova, A. Yu. Semova

The successful application of the CHIM method in the aureole version for exploration of deep-seated gold deposits is dependent to a significant degree upon the effectiveness and quality of analyzing the field samples. The difficulties which arise in this regard are due to the small quantity of gold in the rocks and ores. This results in interference effects from other elements extracted together with the gold. Several techniques have been developed to overcome the problem.

The primary type of analysis for CHIM samples is film polarography with accumulation [I] providing for a low detection limit. In order to record peaks involving nanogram quantities of gold, one can select polarography regimes and appropriate backgrounds allowing as low as 0.001 microgram of gold in the reference solution to be registered. The dependence of the height of the gold peak upon the concentration of gold in a pure solution without the presence of interferring elements is shown in Fig. 1. The polarographic background was 0.1 N hydrochloric acid of chemical purity. The potential of the gold solution was +0.85 V.

The graphs shown were obtained under maximally pure conditions for analysis. It follows from the graphs that polarography with accumulation can be used to determine gold in quantities of 0.001-0.003 micrograms. When interferring compon ents are present in actual CHIM samples, however, the practical limit for gold detection can be found only after investigating the influence of extraneous elements on the results of the gold determination. We chose to study heavy metals in this regard, since they are most likely to be present in solutions of CHIM samples and most likely to have an effect upon gold determination. The studies showed that the widths and amplitudes of the maxima associated with gold-dissolving electric currents when the gold concentration is 0.01 microgram are unaltered in the presence of 1 microgram of Pb, 0.5 micrograms of Fe, 0.6 micrograms of Hg, 0.5 micrograms of Ag, 0.05 micrograms of As, 0.02 micrograms of Sb, and 0.01 micrograms of Cu in 1 ml of solution. An increase in the concentration of each of the elements mentioned leads to a decrease in the heights of the polarographic maxima associated with gold-dissolving currents. Within CHIM samples, the actual concentrations of the elements mentioned are substantially higher than those presented. It is necessary, in this connection, to carry out a selective separation of gold from other elements interferring with the gold determination.

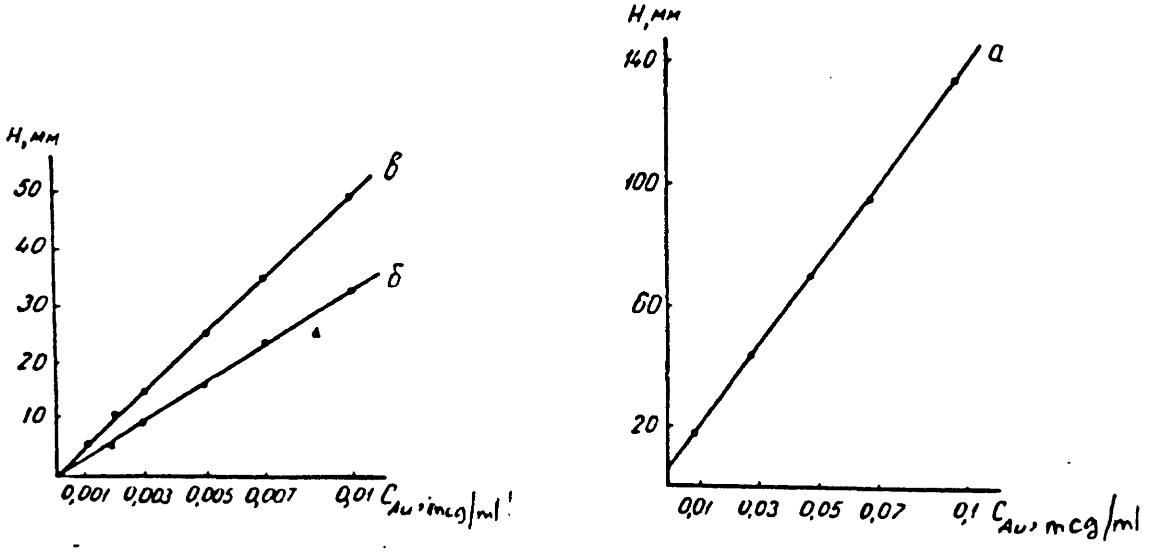

Fig. 1. Diagram of the height of the gold peak versus the concentration of gold in the solution: settling potential ( $\varphi_a$ )- 0.7 V, the scanning rate for the potential ( $V_\varphi$ )- 1.5 V/min, the settling time ( $T_{prec}$ ): a) $T_{prec}$ - 5 min., b) $T_{prec}$ - 10 min, c) $T_{prec}$ - 15 min.

One of the most simple and effective means of removing impurities is extraction of the gold by organic reagents. Gold is most completely and most selectively separated from other elements by dibutyl sulfide (DBS) and is separated somewhat less well by the ethyl ether of acetic acid (ethyl acetate).

An evaluation of the quality of the extraction is carried out with the use of mixtures of iron and gold solutions with these reagents. When the extraction is done using ethyl acetate, traces of iron can be detected in the extract. When the extraction is done using DBS, iron cannot be detected. Ethyl acetate is more suitable in the operation; it is inexpensive and has no disagreeable odor. It is therefore convenient to use ethyl acetate when small quantities of impurities are involved and to use DBS for the extraction when the samples contain significant quantities of admixture elements. It should be noted that extraction by organic reagents, besides removing interferring impurities, also allows one to concentrate the gold to a smaller degree, thereby improving the sensitivity of the analysis.

It is well known that natural organic complexes with gold are simpler compounds than are complexes with artificial organic extractants [3]. In view of the fact that natural organic compounds, gold itself and inorganic gold complexes, are extracted by the electrical currents into solution of element-receivers, it is necessary to treat the samples prior to chemical analysis so that the gold extracted in the form of natural organic compounds will not be lost. For this purpose, one must break down the compounds and convert them to simple ions by treating the samples with concentrated hydrogen peroxide. Several examples of detection of gold in natural organic compounds after treating the samples with hydrogen peroxide are shown in TABLE 1. Adjustments insuring optimal conditions for oxidation are made first.

TABLE 1.

Determination of Gold without Oxidation and with Preliminary Oxidation by Hydrogen Peroxide

| Determination | Amount of gold, mcg | | | |
|---|---|---|---|---|
| | Sample 1 | | Sample 2 | |
| | w/out treatment | after treatment | w/out | after treatment |
| First | 0 | 0,050 | 0 | 0,030 |
| Second | 0 | 0,060 | 0 | 0,035 |
| Third | 0 | 0,050 | 0 | - |

It follows from the table that a treatment of the samples with hydrogen peroxide satisfactorily breaks down the natural organic compounds of gold and allows one to avoid a loss of gold during analysis of CHIM samples.

The use of extraction for the removal of impurities and the concentration of gold lead to the necessity of breaking down the artificial organic complex containing the gold and converting it to a background solution for polarography. Several variants of the decomposition process have been tested [2]. To keep the gold from escaping during the treatment and at the same time to oxidize it completely to the trivalent state, the organic layer was concentrated by evaporation with the addition of sodium chloride after the extraction. The dry sediment was treated with a mixture of hydrochloric and nitric acids in a 3:1 ratio with the addition of 30% hydrogen peroxide. Nitric oxides which would interfere with the polarography are removed by a further addition of concentrated hydrochloric acid twice. The polarographic analysis itself is carried out in a deci-normalized solution of hydrochloric acid.

The procedure for analyzing CHIM samples for gold:

1. The volume of the sample is measured. The sample is evaporated in a thermostable beaker until the volume reaches 10-20 ml. During the evaporation, 5 ml of 30% hydrogen peroxide is added.

2. When cooled to room temperature, the sample is quantitatively transferred to a separatory funnel.

In the case of extraction with ethyl acetate, 5 ml of concentrated HCl and 10 ml of ethyl acetate are added and the extraction is allowed to proceed for 1 min. The aqueous layer is discarded, but the organic phase is washed with 10 ml of 0.1 N hydrochloric acid for 30 sec.

When doing the extraction with dibutyl sulfide (DBS), 10 ml of concentrated HCl is added to the funnel; the mixture is then diluted to 100 ml with water. Next, 3 ml of a 0.1 molar solution of DBS in toluene (freshly prepared) is added and extraction is allowed to proceed for 3 min. An additional 3 ml of DBS is added after the extraction and the solution is mixed. The aqueous layer is poured off and the organic layer is washed twice with 50 ml of 0.1 N HCl for 1 min each time.

3. The organic phase is placed in a thermostable beaker, 3 drops of a 2% solution of sodium chloride is added, and the mixture is evaporated to dryness in a water bath.

4. To the dry residue in the hot beaker, 0,5 - 1,5 ml of a mixture $HCl:HNO_3 = 3:1$ (freshly prepared) is added along with 3 drops of 30% hydrogen peroxide.

When performing the extraction with ethyl acetate, the mixture obtained is evaporated in a water bath to the point of moist salts. To these salts, 0.5 ml of concentrated HCl is added, and the sample is evaporated to dryness. The operation is repeated twice.

When performing extractions using dibutyl sulfide, the mixture is evaporated to dryness. The samples are then treated twice by adding 1 ml of concentrated HCl each time, and the samples are evaporated to dryness.

5. The residue obtained is flooded with the polarographic background (2 ml of 0.1 N HCl), cooled, transferred to an electrolytic cell and subjected to polarography.

6. The polarographic determination is conducted in two regimes:

- sedimentation ( settling ) time 10 or 15 min, depending upon the anticipated gold content;

- sedimentation ( settling )potential 0.7 V;

- rate of scanning of potential 1.6 V/min;

- limit of current recorded 2 mcA.

The working electrode (graphite) is cleaned mechanically prior to each analysis. Auxillary and reference electrodes are silver chloride.

The gold peak is fixed at +0.85 V.

7. The gold content is located on a calibration graph that shows how the height of the peak changes depending upon the gold content in the solution.

TABLE 2.

Reproducibility of Repeated Observations Using the CHIM Method (Au in the sample volume, mcg)

| Regions | Determinations | | |
|---|---|---|---|
| areas | 1 | 2 | 3 |
| Rudnyi Altai | 0,030 | 0,012 | - |
| Area 1 | 0,020 | 0,030 | - |
| | 0,015 | 0,016 | - |
| | 0,012 | 0,014 | - |
| | 0,005 | 0,006 | - |
| | 0,018 | 0,017 | - |
| Area 2 | 0,015 | 0,010 | - |
| | 0,012 | 0,020 | - |
| | 0,007 | 0,009 | - |
| Uzbekistan | 0,021 | 0,032 | - |
| | 0,005 | 0,005 | - |
| | 0,030 | 0,025 | - |
| | 0,007 | 0,005 | - |
| | 0,010 | 0,028 | - |
| Yakutiya | 0,035 | 0,040 | - |
| | 0,038 | 0,040 | - |
| | 0,090 | 0,075 | 0,165 |
| | 0,080 | 0,090 | - |
| | 0,040 | 0,050 | 0,060 |
| | 0,075 | 0,090 | 0,140 |

In order to construct the graph, a CHIM sample known not to contain gold is brought from the area being studied, reference solutions with known gold contents are added to it, and the mixtures are carried through the entire course of the analysis.

8. In order to avoid errors arising from contamination of the reagents used, analysis of a "blank" sample is performed first. Distilled water serves as a basis for the sample. The reagents to be used are added in the sequence provided for by the course of the analysis.

The correctness of the proposed methodology was verified during the analysis of actual samples using the method of additions. The relative standard deviation did not exceed 30% over the entire range (0.005-0.1 mcg) of gold contents studied. The reproducibility associated with repeated observations, including electrochemical extraction of gold along parallel profiles separated from one another by 3-5 m, is presented in TABLE 2.

The table shows that the error associated with the major portion of repeated observations under otherwise identical conditions in different regions did not exceed 40% (the deviation was more than 100% at individual points). The discrepancies are related either to departures from the analytical methodology or to errors associated with geochemical leaching. For conditions meeting the requirements for the analysis and the leaching of elements, the error for repeated observations was within a few tens of percents and provided satisfactory delineation of gold-bearing zones.

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# GOLD EXPLORATION IN SOUTHERN YAKUTIYA USING THE CHIM METHOD

A. A. Veikher

Two types of gold deposits are common in Yakutiya: high sulfide gold veins and the mineralized beds associated with them (the Lebedinsky type), and gold-enriched weathered crusts, often karst limestones hosting stratiform occurrences of gold covered by unconsolidated overburden (the Kuranakh type). Exploration for both types of deposits utilizes a combination of many geophysical and geochemical methods together with geological mapping and drilling [4]. Electrical methods are usually included among the geophysical approaches when searching for the Lebedinsky type deposits. High-precision gravity surveys and magnetic surveys are used for targets of the Kuranakh type. Over areas with thin unconsolidated overburden (up to 2-3 m), gold-oriented soil survey and other geochemical methods are used together with geophysics. With increasing thickness of overburden, however, surface geochemistry becomes ineffective. Geophysical methods, indirect as they are, generally leave unanswered the question of gold potential in areas of known karsts with electro-conductive zones.

The effectiveness of exploration could be increased by a method allowing for a direct delineation of gold-bearing veins, mineralized beds, and karsts in covered areas. The positive results achieved in the exploration for gold deposits in Kazakhstan and Uzbekistan [1, 2] using the CHIM method present a promising opportunity to test the method's possibilities with respect to gold deposits of Kuranakhskii and Lebedinskii types.[1]

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[1] This project was conducted by the CHIM team of the Sixth Geophysical Expedition of the firm "Yakutgeologiya"; A.T. Indyukov, team chief; N.N. Nikulina, chemist.

## Gold Deposits of the Kuranakh Type.

The district encompassing the group of gold deposits where we carried out the test of the CHIM method is characterized by the following principal geologic features. A thick (up to 600 m) carbonate sequence of the Lower Cambrian age is exposed over most of the district. The carbonates rest on an Archean crystalline basement. The carbonate rocks include interstratification of dolomites, limestones, and calcareous mudstones. A terrigeneous formation (up to 120 m thick) of the Lower Jurassic age lies unconformably upon an eroded and karsted surface of the Lower Cambrian. The rocks are sandstones, conglomerates, and silty shales. The post-Jurassic rocks are Neogene-Quarternary in age and range from several meters to tens of meters in thickness. Mezozoic magmatic rocks occur as isolated dikes, small stocks, and quartz veins of subalkalic composition. The dikes extend for hundreds to thousands of meters and have thicknesses of several meters. A few "sill-like" intrusions confined to the zone of stratigraphic contact between the Cambrian and the Jurassic.

The gold mineralization occurs as metasomatic strata-bound deposits of an essentially potassic feldspar and pyrite-quartz composition formed as a result of hydrothermal replacement of the Lower Jurassic sandstones and the carbonate rocks of the Lower Cambrian. The widespread weathering and oxidation almost completely changed the primary ores. In their present state, deposits of the Kuranakh type are products of weathering. The ore is represented by loose gold-bearing limestones of karst cavities.

The mineralized karst formations consist of gold-bearing unconsolidated sand-clay material and bigger fragments of primary ore bodies - metasomatites. The linear zones of gold-bearing karst are confined to the stratigraphic contact between the rocks of the Lower Cambrian and the siliciclastic rocks of the Jurassic.

The age of the gold-bearing karst carbonates is accepted approximately as Late Tertiary. The karst-forming process, which began at that time, continues into the present [3]. Karst formation in limestones usually begins at the footwall of metasomatized limestones. Highly acidic groundwaters penetrating the carbonate rocks from an oxidation zone of metasomatic rocks lead to dissolution of carbonates. Closed karst cavities are formed as a result. With increasing karst development, the roof rocks cave in, oxidized gold-bearing metasomatites accumulate in the karst cavities along with Jurassic sandstones and conglomerates protected from erosion. Finally, the closed karst cavities transforme into the open ones.

In closed karst cavities, gold occurs in the form of free gold in the size fraction greater than 0.01 mm. The particles of the gold are flaky dendritic or lumpy. Silver, copper, lead, bismuth, iron, and arsenic are present as admixtures in the gold. Aluminum, titanium, manganese, and other elements are also present in small quantities. In the open karsts, some particles of gold are greater than 0.01 mm, but some in the clay fraction are less than 0.01 mm. In the clay fraction, the total content of gold is higher than in the coarser one. The presence of gold in the fine fraction within the open karst cavities is explained by the dissolution of the gold by ground waters during the open-karst stage, with subsequent sorption by clay minerals. Such gold can be present in ionic and colloidal states. In addition to karst cavities, higher gold concentrations have been noted in the soil directly above gold ore bodies where the thickness of the unconsolidated overburden does not exceed 1-2 m in situations involving open karsts [4]. Soils above the closed karst cavities do not contain high concentrations of gold. The CHIM survey was carried out on those mineralized zones where the thickness of overburden does not exceed ~3-5 m. The extraction was carried out at element-receivers with membrane areas of 40 cm². Complications arose when setting up the element-receivers in the soil. It turned out that the top layer of soil, with a depth of 0.1-0.3 m, has very high specific resistivity (from 12,000 to 20,000 Ohm). Such a soil resistivity does not permit the high-power regime necessary for gold extraction. Therefore, the ERs were placed in a second, deeper layer (~0.5 m) possessing a specific resistivity of 200-500 Ohm. These layers can be distinguished visually: the lower layer is denser and clay-rich compare to the upper, sandy layer. The necessary high-power extraction regime was achieved when setting up the ERs in the lower layer with lower resistivity: the electric field strength in the vicinity of the ER is ~2 V/cm at a current strength of 300-400 mA. The extraction time is 10 hours. The results of observations along one of the profiles are presented in Fig. 1. On the graph, one can conditionally distinguish several levels corresponding to different quantities of extracted gold: 0.3-1.0 ppm, 0.1-0.3 ppm and > 0.1 ppm. Maximum extraction of gold (0.3-1.0 ppm) corresponds to the outcrop projections of an ore body to the surface. Less intense anomalies were encountered above dikes containing anomalous gold.

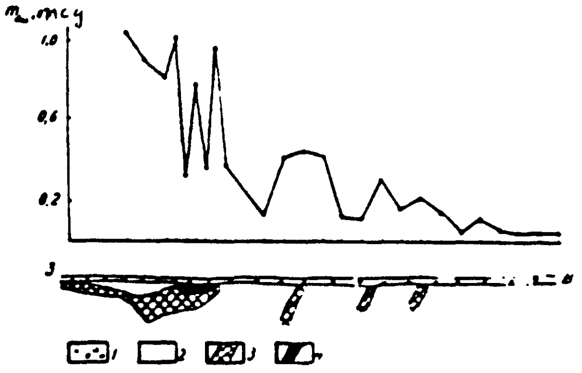

Fig. 1. The CHIM method results for deposits of the Kuranakh type: 1) unconsolidated Quarternary, 2) Lower Jurassic sandstones, 3) dike-related and low grade gold mineralization, 4) gold orebodies.

Thus, the CHIM method satisfactorily delineates the primary ore body and dikes with gold contents either lower than in the primary body or significantly higher than in the country rock.

## Gold Deposits of the Lebedinsky Type.

Rocks of the Archean basement are a part of the geological structure of a district with the Lebedinskii type mineralization. Limestones and dolomites of the Lower Jurassic concordantle overlie the basement structure. The maximum thickness of the carbonate sequence is 200 m. The structure of the area is characterized by many high angle faults. The distribution and occurence of the gold are primarily determined by elements of high angle tectonics - vertical fissure zones in combination with stratabound zones of weakness. Ore bodies represented by steeply dipping quartz-sulfide veins are hosted by the lower Cambrian carbonates. Flat-lying ore bodies occur on several levels. The lower horizon of commercial mineralization is the footwall of the Cambrian limestones at the contact with the crystalline basement. The mineralogy of the ore is quartz, base metal sulphides, hematite and pyrite.

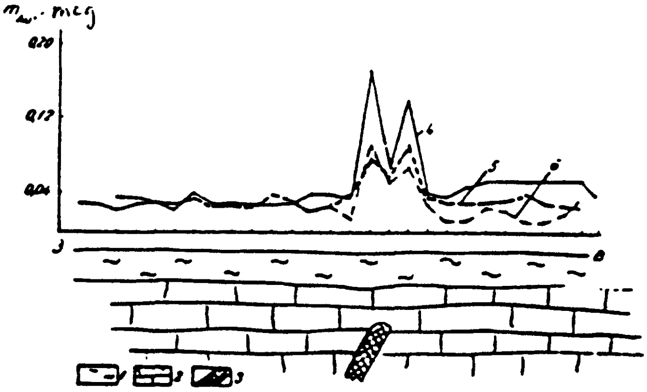

Fig. 2. The CHIM method results for deposits of the Lebedinsky type (Site 1): 1) Quarternary overburden, 2) limestones and dolomites of the Lower Cambrian, 3) gold-sulfide ore zone; gold-extraction curves using the CHIM method: first (4) and repeated (5, 6) observations.

A covered orebody hosted in dolomites at 40 m was successfully identified in a well studied part of the deposit where the CHIM method was used. The gold was extracted into the ERs with a membrane area of 40 cm$^2$. A high-power regime ensuring the current strength through each ER of 300-400 mA and the electric field strength of 2V/cm was set. The extraction time was 10 hours. The results of the experiment presented on Fig. 2 show that an elevated gold extraction was observed directly above the subcrop projection of the orebody onto the surface. The width of the anomaly along the profile was 60 m.

In order to evaluate the reproducibility of the observations, repeated measurements were carried out along the profiles which were offset parallel to the first profile by 2 and 3 m. The extraction regimes were identical. Figure 2 shows that anomalies are reproduced well with respect to width and position on the profile but not with respect to gold levels. In general, the results of the observations show that it is possible to identify gold deposits within limestone host rock at a depth of ~40 m.

At another area with a similar geological environment, gold was extracted along two profiles located 150 m from one another on the slope of a hill. The gold mineralization within Profile I occurs in dolomites and represents two tube-shaped orebodies located close to each other. The ore bodies are blind and overlied by a bed of dolomites. Soils in the area have thicknesses varying from 0.5 to 2 m. At some places, the soils are rubbly containing coarse rock fragments. The element-receivers were set up along the profile in a humus layer at a depth of 5-10 cm. At locations where a great deal of rubble turned up under the ER, the soil was shifted through a screen with a 2-mm mesh and then moistened with distilled water. The gold was extracted at a current of 250-400 mA through each ER. The field strength was 2 V/cm. The extraction time was 10 hours for Profile 1 and 20 hours for Profile 2. There were two cycles of testing: 0-10 and 10-20 hours. The results are shown in Fig. 3, where the zone with gold-sulfide ore bodies is satisfactorily delineated by the CHIM method and can be traced well from profile to profile. Another anomaly located to the north of the first one was delineated on the basis of weaker but still satisfactory gold extraction. It corresponds to an unexplored gold mineralization intercepted by only a few drill holes and trenches. This new zone, as in the case of the first well studied zone, can be traced well from Profile I to Profile 2.

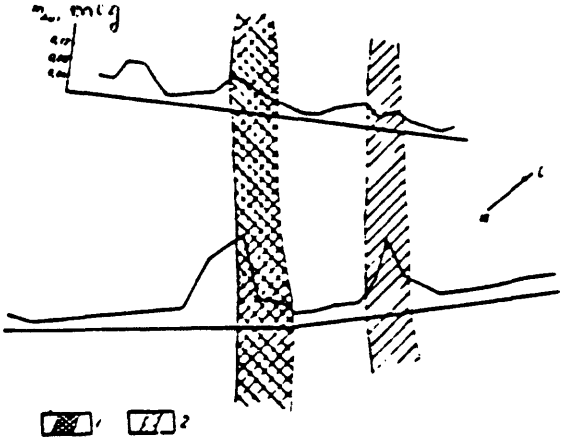

Fig. 3. The CHIM method results for deposits of the Lebedinsky type (Site 2): 1) well studied zone of gold mineralization, 2) new ore zone known from a few trenches and intercepted by drill holes.

In addition to these two anomalies, there is still a third anomaly located on Profile I to the south of the well studied ore zone. Its nature is unclear. It is possibly caused by an old mining road passing through the area, but it could be associated with unknown mineralization and requires special study. It should be first traced by the CHIM survey along the strike.

Not counting this third anomaly, the data obtained indicate a satisfactory identification of the gold mineralization of the Lebedinsky type by the CHIM method.

On the whole, the developmental work using the CHIM method for identification of a gold mineralization in Yakutiya shows the possibility of delineating gold anomalies under a cover up to 40-m thick . It could also be noted that the mass of gold extracted by the CHIM method was significantly greater than that extracted in Eastern Kazakhstan and Uzbekistan.

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