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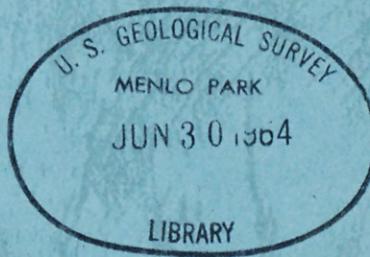
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Determination of ammonium citrate-soluble cobalt
in soils and sediments

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F. C. Canney and G. A. Nowlan





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Determination of ammonium citrate-soluble cobalt
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By F. C. Canney and G. A. Nowlan

Abstract

A rapid field method for the determination of cold-extractable cobalt in soils and sediments has been developed for use in geochemical prospecting. Readily available cobalt is dissolved by treating the sample with an aqueous ammonium citrate-hydroxylamine hydrochloride solution; the filtered citrate extract is then treated with 2-nitroso-1-naphthol to form a pink-colored cobalt complex which is concentrated in a floating organic layer by a 1 to 3 mixture of carbon tetrachloride and cyclohexane. After the organic extract is shaken with potassium cyanide solution to eliminate interference by copper and nickel, the intensity of the pink to red color is estimated by comparison with a standard series.

A concentration range of 1 to 60 ppm is obtained when a 0.2-g sample is used but this range is varied easily by adjustment of sample size and volume of organic solvent. A minimum of 100 determinations per 8-hour day can be made, and because only simple, readily portable items of equipment are required, the method is adapted to use under rough field conditions, at the sample site if desired.

Introduction

Dispersion patterns of citrate-soluble cobalt in stream sediments have recently been found to be a useful guide in searching for mafic rocks mineralized with cupriferous, nickeliferous, and cobaltiferous sulfides. The well-known and widely used citrate-soluble heavy metals procedure (Bloom, 1955; Ward and others, 1963, p. 27-29) was originally used to estimate extractable cobalt, but the sluggishness of the cobalt-dithizone reaction makes it extremely difficult for even an experienced analyst to obtain reproducible data. And the lack of specificity of the method makes it difficult to correlate the data of a survey with the cobalt content of samples unless the zinc and copper background is reasonably constant. Thus a specific test for cold^{1/} extractable cobalt presumably would be useful in geochemical prospecting surveys.

1/ "cold" means extraction by ambient-temperature solutions.

The aim of our investigations was to produce a test that was specific for cobalt and yet had the speed and basic simplicity of the various other cold-extractable methods in current use. And also, as far as possible, we wanted to use reagents, extractants, and apparatus that are in common use in geochemical prospecting analytical methods today. Accordingly the cobalt method described here combines some features and uses some reagents of the citrate-soluble heavy metals test (Bloom, 1955) and the procedure for the determination of total cobalt (Almond, 1953; Ward and others, 1963, p. 34-35). Although this method requires more manipulations than the other cold-extraction methods, it is still quite fast. One man can make 100 determinations easily in an 8-hour day, and more if a scooped sample is used. The method is also readily adapted to use under rough field conditions, at the sample site if desired.

The procedure is based on the reaction of cobalt with 2-nitroso-1-naphthol to form a pink compound soluble in many organic solvents. In the method: (1) available cobalt is first dissolved by the citrate extractant; (2) an aqueous solution of 2-nitroso-1-naphthol is added to form cobalt 2-nitroso-1-naphtholate; (3) the cobalt 2-nitroso-1-naphtholate is dissolved and extracted into a floating organic layer by a 1 to 3 mixture of carbon tetrachloride and cyclohexane; (4) addition of a cyanide solution and further shaking eliminate any possible interference by copper and nickel and also remove any yellow color caused by the solution of some 2-nitroso-1-naphthol reagent in the organic extractant; and (5) a light-pink to dark-red solution results in the organic layer that is proportional to the amount of readily soluble cobalt.

Reagents and apparatus

It is assumed that most users of this method are familiar with the basic laboratory equipment that must be available in a geochemical laboratory. Accordingly, no attempt has been made to list the items of regular laboratory equipment that are required to prepare the reagents and standards. Only some items specifically required are mentioned in the procedure. Those individuals who need additional information should consult Ward and others (1963).

Ammonium citrate-hydroxylamine hydrochloride extractant, concentrated

stock solution: Dissolve 400 g ammonium citrate $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$) and 64 g hydroxylamine hydrochloride $(\text{NH}_2\text{OH}\cdot\text{HCl})$ in about 1200 ml water.

Add concentrated ammonium hydroxide (NH_4OH) until testing with pH paper shows that the solution has a pH of about 7. Place the solution in a separatory funnel and remove heavy metals by extraction of the aqueous solution with 100-ml portions of a carbon tetrachloride (CCl_4) solution of dithizone (0.01 percent) until the carbon tetrachloride layer remains green. Extract the dissolved dithizone by shaking the aqueous solution with 100-ml portions of chloroform (CHCl_3) until the chloroform is colorless. Then wash twice with 100-ml portions of CCl_4 to remove dissolved CHCl_3 .

Finally dilute to 2 ℓ with metal-free water.

Ammonium citrate-hydroxylamine hydrochloride extractant, working solution: Dilute 1 volume conc. stock solution with 3 volumes metal-free water. Check the pH of the solution with pH paper and adjust to 8.5 with metal-free NH_4OH .

2-nitroso-1-naphthol reagent solution, 0.01 percent: To 0.05 g

2-nitroso-1-naphthol add 10 drops of 2M sodium hydroxide (NaOH).

Add metal-free water slowly in increments of 2-3 ml to a volume of about 20 ml while mixing with a glass rod. When the reagent is completely dissolved, dilute to 500 ml with metal-free water.

Potassium cyanide solution, 10 percent: Dissolve 100 g potassium cyanide (KCN) in water and dilute to 1 liter with metal-free water. (CAUTION, POISON: do not measure a cyanide solution with a pipet operated by mouth. Do not add acid to cyanide solutions.)

Organic solvent: Mix 250 ml carbon tetrachloride (CCl₄) with 750 ml cyclohexane (C₆H₁₂).

Standard cobalt solution, 100 μ g per ml: Dissolve 0.04 g cobalt chloride (CoCl₂·6H₂O) in metal-free water, add 1 ml conc. hydrochloric acid, and dilute to 100 ml in a volumetric flask. From this solution prepare more dilute standard solutions (10 μ g per ml and 1 μ g per ml) just before preparing standards.

Ammonium hydroxide, conc., reagent-grade.

Ammonium hydroxide, approx. 4N, metal free: Prepare by dissolving ammonia (NH₃) in metal-free water.

Carbon tetrachloride (CCl₄), reagent-grade.

Chloroform (CHCl₃), reagent-grade.

Dithizone solution, 0.01 percent in carbon tetrachloride (CCl₄):

Dissolve 0.05 g dithizone (diphenylthiocarbazone) in 500 ml of CCl₄.

Procedure

The following procedure is described in terms of a single sample but batch operation is normal except at the sample site. When batch operation is used, however, it is critical that the contact time between the sample and citrate extractant be closely controlled. Thus this phase of the method should be done on individual samples or small groups of six or less. Once the sample has been separated from the citrate extractant by filtration, however, timing is not critical and large batches of sample solutions can be accumulated before the remaining steps of the procedure are carried out. Additional remarks about some of the chemistry involved and the reasons behind some of the manipulations are presented in the discussion.

1. Weigh 0.2 g or take a 0.2 cc scoopful (0.1 g or 0.1 cc will extend the concentrational range upward) and tap into a 22- X 175-mm test tube.
2. Add 10 ml citrate extractant (working solution) to the tube, slosh for 15 seconds, and immediately filter solution through a filter paper (Whatman no. 41, 11 cm in diameter) into another 22- X 175-mm test tube.
3. Add 3 ml of 2-nitroso-1-naphthol reagent to the filtered solution and mix the contents.
4. Add 2 ml organic solvent, cap the tube, and shake vigorously for 30 seconds.
5. Add 2 ml potassium cyanide solution and shake for about 10 seconds.

6. When the layers separate, compare the color in the floating organic layer with the colors of similarly prepared standard solutions of known cobalt content. Centrifuging the tube aids in the separation of the phases and helps break up any emulsification in the organic phase.
7. Calculate the content of readily extractable cobalt according to the following formula:

$$\text{parts per million (ppm)} = \frac{\text{micrograms } (\mu\text{g}) \text{ of cobalt found}}{\text{sample weight (g) or sample volume (cc)}}$$

Results are expressed as ppm weight/weight if a weighed sample is used; ppm weight/volume if a scooped sample is used.

A series of cobalt standards for 0, 0.2, 0.4, 0.8, 1.5, 3.0, 6.0, and 12.0 μg of cobalt is recommended. To prepare the standards, place 10 ml of the ammonium citrate extractant in each of a series of 22- X 175-mm test tubes, and add to each the required amount of standard solution (μg per ml and 10 μg per ml), to produce the series suggested above. Mix thoroughly and filter each solution through filter paper as in step 2 and then follow the regular procedure starting with step 3. These standards should be kept tightly capped to prevent evaporation of the organic solvent and a resultant intensification of the color.

Discussion

The following sections are for those analysts who are interested in the chemistry involved and the reasons for the various manipulative steps. They will be of especial value to those who may be required to modify the method to meet unusual conditions, types of samples, or unavailability of some of the reagents specified.

Reagents and standards

All reagent solutions are stable at room temperature for long periods. The organic extracts of the cobalt 2-nitroso-1-naphthol complex also show excellent color stability. Provided that tubes are tightly capped, a standard series should be usable for at least several weeks. An apparent very slight intensification of the color is occasionally noticed about 24 hours after preparation of a standard series. This change is believed due to the gradual clearing of opalescence caused by a dispersion of water droplets in the organic phase; no significant error is introduced thereby, however.

About 2 to 2.5 ml of sample solution is retained by the filter paper and sample when the citrate sample extract is filtered. This loss of cobalt-bearing solution is adequately compensated for, however, by also filtering each standard solution during the preparation of a color comparison series.

Concentration range

The concentration range of the method is 1 to 60 ppm when a 0.2-g sample is used and 2 to 120 ppm for a 0.1-g sample. If desired the upper limit of the method can be raised by use of a larger volume of organic solvent or by use of a sample weighing <0.1 g. Conversely the lower limit can be decreased slightly by increasing the sample size to 0.4 or 0.5 g or by decreasing the volume of organic solvent. The use of a 1-ml volume of organic solvent is near minimal, however, for satisfactory color comparisons.

When using the method as described, the analyst can often measure the cobalt content of the occasional sample that exceeds the upper limit of the standard series without rerunning the sample by adding another volume or two of the organic solvent and shaking the tube briefly. In such instances, of course, an appropriate dilution factor should be applied in the formula used to calculate the cobalt content.

Estimation

The principal difficulty in making color comparisons is the frequent presence of a persistent emulsion in the organic phase. This emulsion is apparently caused by organic matter leached from the sample. We have found no really satisfactory solution thereto. Although Marshall (1964, p. 145) reports the use of silicone antifoam reagents effective in preventing emulsification, our trials with reagents of this type were unsuccessful. As mentioned in the procedure, centrifuging helps significantly and is recommended if equipment is available. Otherwise, allowing the organic extracts to stand for a short time prior to estimation is often helpful, as the emulsion gradually breaks down during standing.

Extraction of cobalt from the sample

The necessity for closely controlling the time of contact between the sample and the ammonium citrate-hydroxylamine hydrochloride extractant has been mentioned. Normally the amount of metal extracted from a sample increases with time of contact between sample and extractant. Variability in the time of extraction is a well-recognized major source of error in the cold-extractable field tests. In this method, however, our principal concern with this point arises from the fact that the content of extractable cobalt--at least the amount capable of reacting with 2-nitroso-1-naphthol--is at a maximum for only a short period after extraction. Thereafter the apparent content of extractable cobalt decreases erratically if the sample material is allowed to remain in contact with the citrate extractant. The rate of decrease varies both with time and from sample to sample. We found that the amount of extractable cobalt remained constant at its initial high level, however, if the sample was immediately separated from the citrate extractant by filtration or decantation. The reason for this behavior is not completely clear but we suspect that organic matter is slowly leached from the sample and combines with part of the already dissolved cobalt to form a complex that is not decomposed by the 2-nitroso-1-naphthol reagent. Credence to this assumption is given by the marked decrease with time in reactive cobalt by those sediment samples having the highest content of organic matter.

An attempt was made to avoid filtration by adding the cobalt reagent and organic solvent immediately after the citrate extraction but it was not successful. Much lower values were usually obtained than for solutions from which the solids had been separated. Adsorption of the cobalt 2-nitroso-1-naphtholate on the sample appears to be a possible cause.

Organic solvent

Our study of the effectiveness of various organic solvents was not exhaustive and probably a number of other solvents would be as satisfactory as the 1 to 3 mixture of carbon tetrachloride and cyclohexane specified here. The principal criteria used in judging the effectiveness of various organic solvents were: 1) speed of separation of the organic and aqueous phases, 2) minimum solubility of the organic solvent in the citrate extractant, 3) minimum solubility of the 2-nitroso-1-naphthol, and 4) maximum solubility of the cobalt 2-nitroso-1-naphtholate. Also, because of the more efficient viewing geometry when color comparisons are made in a test tube, a lighter-than-water solvent was preferred.

We tried the following solvents: Xylene, isoamyl acetate, ethyl acetate, cyclohexane, n-butyl benzoate, isoamyl alcohol, carbon tetrachloride, n-hexane, benzene, toluene, 1-chlorobutane, 4-methyl-2-pentanone, nitrobenzene, n-octane, and a 1 to 3 mixture of carbon tetrachloride and cyclohexane. The last-mentioned solvent was judged best, according to the four stated criteria. The addition of 1 part carbon tetrachloride increases the solubility of the cobalt

2-nitroso-1-naphtholate. Some 2-nitroso-1-naphthol reagent does dissolve in this mixture initially but the cyanide extraction removes all traces of the interfering yellow color. The reagent's solubility in the organic solvent is not sufficiently great, however, to permit a direct extraction.

Interfering elements

Under the conditions of the test, copper and nickel also react with the reagent and are at least partially extracted along with cobalt 2-nitroso-1-naphtholate. In the absence of the cyanide solution 10 μ g each of copper and nickel produced colors in the organic layer that slightly modified the color of the pink cobalt complex in the lower ranges of a cobalt standard series but the interference was judged not to be serious. Higher amounts (30 μ g), however, produced a precipitate that collected at the interface of the organic layer. The addition of the cyanide, however, eliminates any interference due to copper and nickel but does not decompose the cobalt 2-nitroso-1-naphthol complex. We wish to emphasize that the cyanide should be added only after the cobalt 2-nitroso-1-naphthol complex has been formed, as the complex will not form in the presence of cyanide.

Clark (1958, p. 1155) stated that manganese (II) inhibits formation of the cobalt 2-nitroso-1-naphthol complex. However, no interference was noted when 0.8 μ g of cobalt was determined in the presence of 15,000 μ g of manganese, and we conclude that manganese is unlikely to interfere under the stated operating condition.

Ferrous iron also interferes by forming a green precipitate that collects at the interface between the aqueous and organic phases. However, in practice we have yet to observe such interference even though some of our samples had high iron content. Should such interference be noted, the sample should be reanalyzed and bromine water or hydrogen peroxide added to the citrate extract prior to addition of the 2-nitroso-1-naphthol reagent.

Interference by tin and palladium, which are also reported by Clark (1958, p. 1155) to form complexes with 2-nitroso-1-naphthol, is considered unlikely due to their low abundance in soils and sediments.

Elimination of the cyanide extraction

Although the cyanide extraction is recommended and included in the procedure for the reasons given, it could be eliminated if only a quick sorting procedure was needed to detect highly anomalous samples, or if it was desired to use the procedure at the sample site. The degree of interference by copper, nickel, and dissolved reagent in the organic layers is not sufficient to prevent recognition of an anomalous sample.

Reproducibility

Replicate analyses of a group of 40 samples with cold-extractable cobalt values well distributed between 1 and 120 ppm provided the data in the following tabulation by which the reproducibility of the method can be evaluated.

Agreement between duplicates within a factor of	Number of samples
1 (perfect agreement)	16
1.5	32
2	39

This is considered a satisfactory level of precision.

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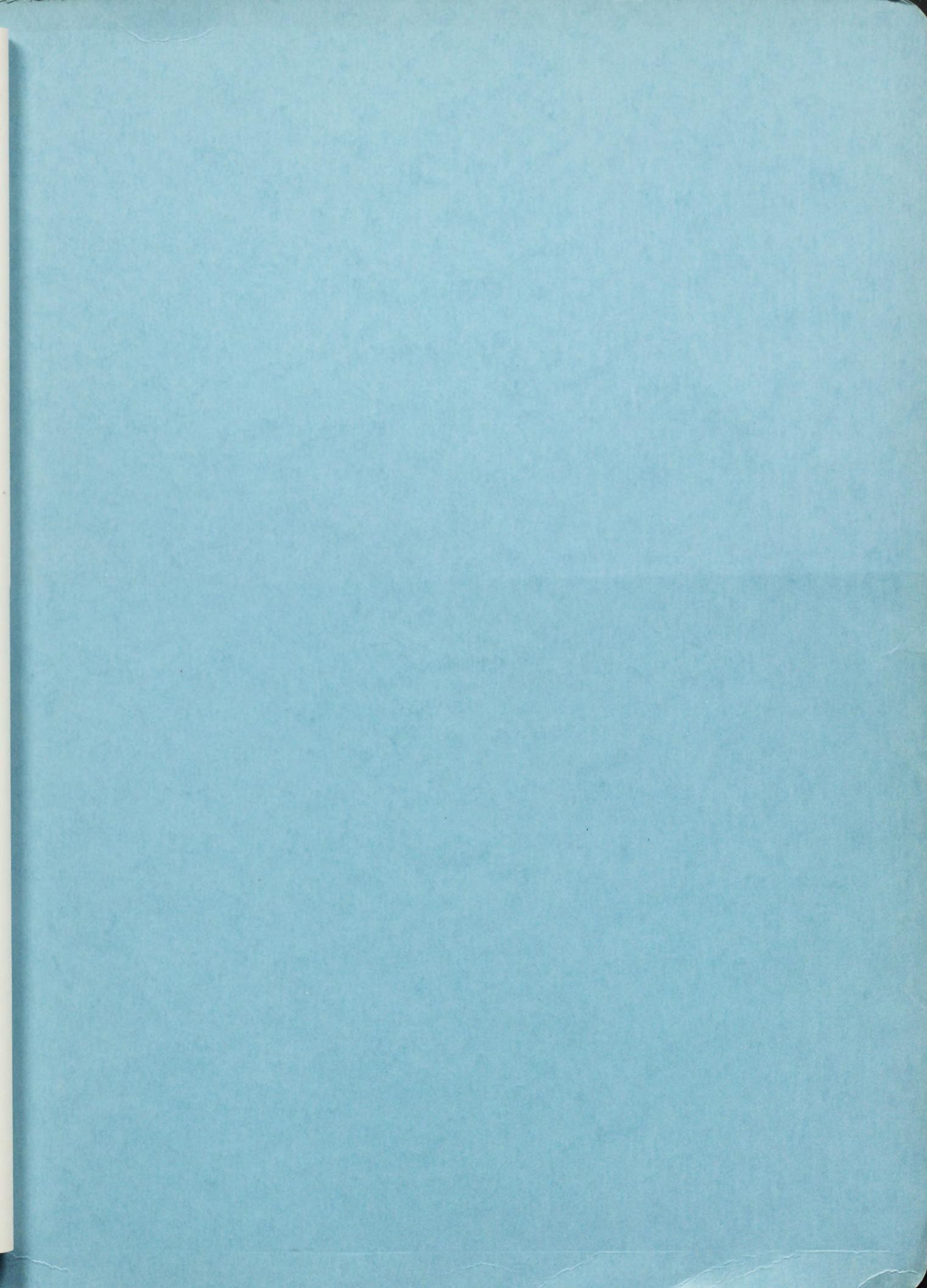
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