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ANALYSIS OF BROMINE IN BRINES USING ENERGY DISPERSIVE X-RAY FLUORESCENCE

by

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ABSTRACT

Water samples, mainly brines, whose bromine content varied two orders of magnitude were collected in the Eastern Province of the Kingdom of Saudi Arabia. Easily available wet-chemical and colorimetric methods of bromine analysis were not found suitable and an analytical method of bromine analysis using energy dispersive X-ray spectroscopy was developed. No timed reactions and little sample manipulation are required, and the method can be used by a semi-skilled technician. The method has a limit of detection of about 3 mg/l and a limit of determination of about 16 mg/l. It is suitable for use on waters of widely varying salinities that have compositions dominated by sodium and chloride ions.

INTRODUCTION

The United States Geological Survey conducted a water sampling program in the Eastern Province of the Kingdom of Saudi Arabia in order to develop geochemical methods of exploration for shallow halite beds. Most of the samples were brines collected from coastal and continental sabkhas. These water samples were analyzed for ions such as calcium, magnesium, sodium, potassium, chloride, sulfate, and bicarbonate, which constitute a major portion of the solutes, and for other ions such as lithium, fluoride, and bromide.

Bromine is an important element in geochemical studies of evaporite deposits because it does not form minerals independently of other bases but instead substitutes for chlorine in evaporite mineral lattices. The concentration of bromine in a chlorine-containing evaporite mineral is a predictable function of the bromine concentration of the brine from which the mineral was precipitated.

There are several methods for measuring bromine concentration in natural waters (Balatre, 1936; Fishman and Skougstad, 1963; Goldman and Byles, 1959; Holser, 1966; Kolthoff and Sandell, 1952; Rose and Cuttitta, 1968; Shiota and others, 1959; Stenger and Kolthoff, 1935). The most popular methods of bromine analysis in natural waters are neutron-activation analysis and the wet chemical or colorimetric methods that include a step in which bromide and(or) iodide are oxidized to bromate and iodate. These methods have often been tested for use on water of low ionic strength. Neutron activation, because of its great sensitivity, has been used to analyze rain and snow to determine their bromine concentration (Duce and others, 1965). Balatre (1936) devised a colorimetric procedure to measure bromine concentration in blood. Holser (1966) modified this procedure in an unspecified manner and applied it to brines. These methods are very similar to that presented in the handbook "Standard methods for the examination of water and wastewater" (American Public Health Association and others, 1974) which referenced Stenger and Kolthoff (1935) and Goldman and Byles (1959). All these methods determine bromine abundances by forming bromate in a buffered solution containing phenol red and chloramine-T. After the solution is dechlorinated, the color intensity is measured at a particular wavelength using a spectrophotometer.

As with most analytical techniques, there are disadvantages to using these conventional procedures. One of the most serious impediments to using neutron-activation analysis is the necessity of using a nuclear reactor. Also, the high total dissolved solids in brines can cause absorption-enhancement effects. The wet-chemical methods of bromine analysis require rather extensive sample preparation and sometimes involve timed reactions. In addition, these wet-chemical procedures can only determine bromine quantitatively when its concentration is in a narrow range. If a sample set contains samples in which bromine concentrations vary two orders of magnitude or more, several dilutions may be necessary to bring the bromine concentrations into the correct range. These conditions make the wet chemical methods difficult for semi-skilled technicians and chemists to perform.

X-ray spectroscopy is another analytical method that can be used to analyze for bromine in brines (Jackson and Powers, 1977; Rose and Cuttitta, 1968). With energy-dispersive X-ray spectroscopy it is possible to determine the presence of chemical elements in a sample by inducing the sample to emit radiation during exposure of the sample to X-rays or gamma rays. The energy spectrum of the emitted radiation is characteristic of the elements present in the sample. The X-ray analytical method presented here for analyzing bromine in brackish waters and brines has many of the advantages inherent in X-ray techniques. The method requires little sample preparation, is relatively quick to perform, is nondestructive, has the potential to obtain quantitative information on more than one element simultaneously, and is able to analyze bromine over a wide concentration range without sample dilution.

APPARATUS

The energy dispersive x-ray fluorescence spectrometer used in this study is a Kevex Micro-X 7000 analytical spectrometer with a microprocessor-based electronics mainframe and a control console with color-coded video display. The apparatus includes a Kevex series 3000 cryogenic subsystem with a lithium-drifted silicon detector head assembly, a cryostat with beryllium window, a charge-sensitive preamplifier, and a liquid nitrogen Dewar flask. The general system uses, a floppy disk drive, a printer, and Fe^{55} (100 miC), Cd^{109}(20 miC), and Am^{241} (20 miC) as excitation sources. X-ray mylar film, 6.3 microns thick, was used in conjunction with closed-cell polypropylene x-ray sample cups 30 mm in diameter.

EXPERIMENTAL PROCEDURE

Suprapur (trade name of E. Merck) NaCl was used in the preparation of matrices of the bromine standards. The standards were prepared using reagent grade KBr. Bromine standards containing 0, 24.4, 47.6, 123.5, 244, and 476 mg/l bromine were prepared in matrices of 0, 7010, 35100, 70200, 104000, 144000, 179000, and 234000 mg/l NaCl. Both standards and samples were prepared for analysis by pipetting 2 ml into a polypropylene cup and sealing it with mylar film. An aluminum cap was placed over the sample or standard so it was between the lead shielding of the sample chamber and the radioactive Cd^{109} source after the sample was rotated into position for analysis.

A spectrum of a standard containing 234000 mg/l NaCl with no added bromine, subsequently referred to as a blank, was accumulated for 100 live seconds and stored in the first quarter of the memory of the multichannel pulse-height analyzer. This spectrum was moved to the second quarter of the multichannel analyzer memory and erased in the first quarter of memory. A second spectrum of the blank was then acquired for 6000 seconds in the first quarter of memory and normalized with respect to the spectrum stored in the second quarter of memory. The normalization was accomplished using an energy window, with an energy range from 1.48 keV to 2.04 keV. The normalized spectrum was then transferred both to the second quarter of memory and to storage on a floppy disk and became the spectrum against which all subsequent sample and standard spectra were normalized. The subsequent sample and standard spectra were acquired for 100 to 500 live seconds. After normalization of a sample or standard spectrum, the blank spectrum was subtracted from the spectrum. This procedure removes most of the displayed background from sample and standard spectra and leaves well-defined bromine peaks if there is sufficient bromine present.

The residual counts were printed from a window in which the energy ranged from 11.64 keV to 12.20 keV, and which bounds the bromine Kα peak. The bromine Kα peak intensity of the sample was then compared with that of standards containing a similar NaCl concentration, and a bromine concentration of the sample was estimated.

DISCUSSION

Water samples analyzed for bromine were collected in and near sabkhas in the Eastern Province of the Kingdom of Saudi Arabia. They varied in composition from relatively fresh waters to brines with bromine concentrations ranging from less than 5 mg/l to over 500 mg/l. The dominant cation in these waters is sodium and the dominant anion is chloride (fig. 1). Because of the nature of the USGS evaporite project, most of the samples collected in the Eastern Province were brines.

Attempts were made to analyze the waters for bromine using the wet-chemical method described in the handbook "Standard methods for the examination of water and wastewater" published by the American Public Health Association and others (1974). Using the chloramine-T method of analysis described in that handbook, two USGS-DGMR chemists independently attempted to analyze 145 natural water samples for bromine. The results of analyzing duplicate samples collected at the same sample locality and at essentially the same time indicated the chloramine-T method, when used by our chemists, did not give satisfactory precision. The difficulties experienced by our chemists prompted the development of the method of analysis presented here. Table 1 compares the results of the chloramine-T method on duplicate samples with the results of the x-ray fluorescence technique described in this paper. While it is not certain if the poor precision of the chloramine-T analytical results is due to an intrinsic lack of precision of the method, the analytical results of duplicate samples indicate the method is not appropriate for use with samples containing highly variable total dissolved solids and relatively high bromine concentrations under the conditions present in our laboratories.

The sample preparation and analytical procedures of the energy-dispersive x-ray fluorescence method presented in this paper are much simpler than those necessary for wet-chemical techniques. Sample preparation consists of transferring 2 ml of sample or standard solution to the closed-cell polypropylene cups and sealing the cups with mylar film. It is not necessary to transfer exactly 2 ml since the intensity of the Kα bromine peak was found to be independent of sample volume when sample volume was over 2 ml (fig. 2). The Kevex

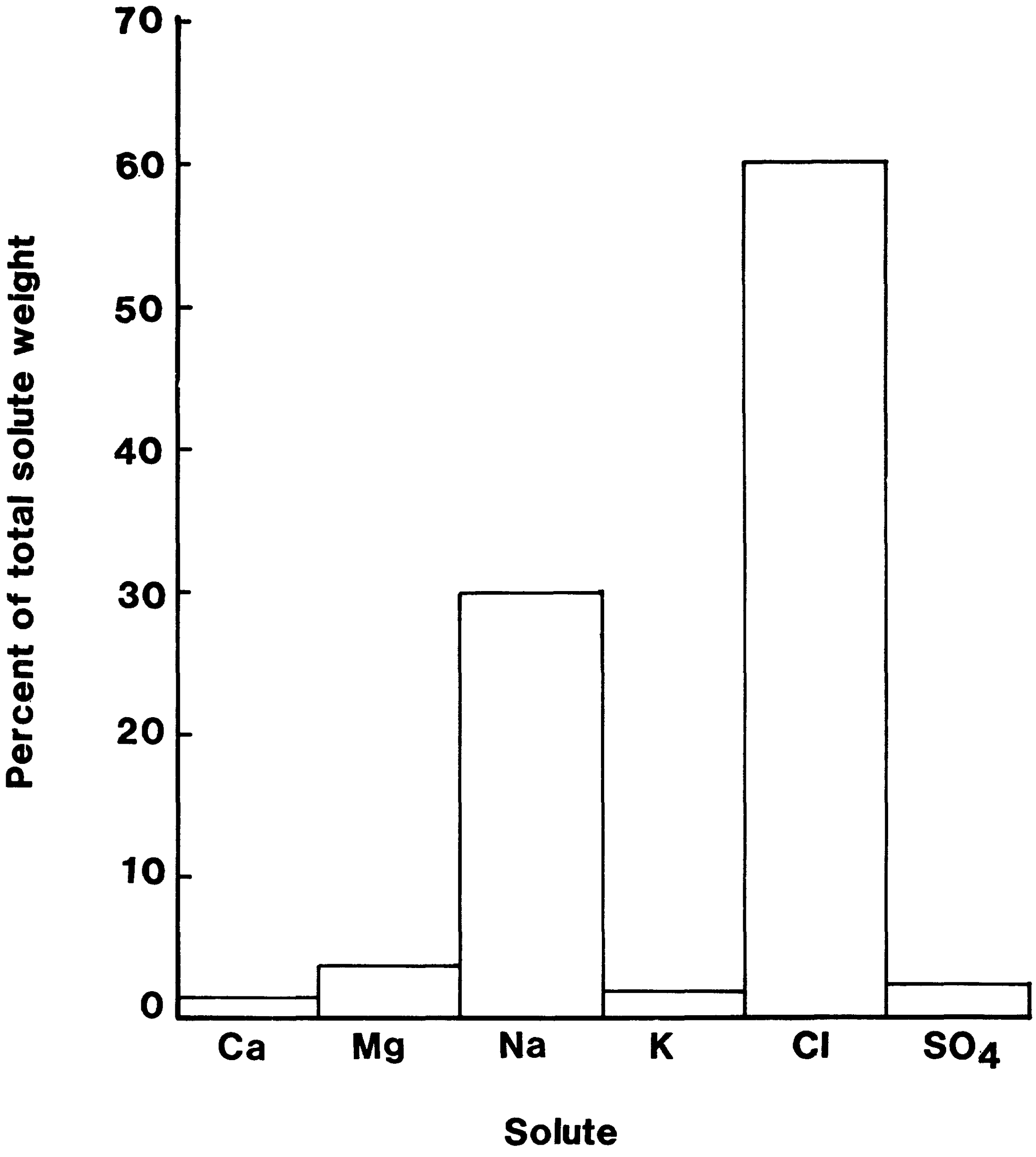

Figure 1.–Relative abundance of those ions which compose over one weight percent of the total solute load of a water sample of average composition. The average composition of the water was determined by averaging the concentration of individual ions in 40 randomly selected water samples from the Eastern Province of the Kingdom of Saudi Arabia.

Table 1.--*Comparison of the chloramine-T and X-ray fluorescence methods of bromine analysis on duplicate samples*

[Duplicate samples used in this comparison were collected at sample sites in separate bottles and submitted in random sequence to two different analysts for analysis by the chloramine-T method of bromine analysis. These samples were also analyzed by the X-ray fluorescence method of analysis. The relative average standard deviation of duplicate samples was calculated by the method of Garrett (1969)]

Sample site	DGMR sample number	Br(mg/l) determined by analyst 1	Br(mg/l) determined by analyst 2	Br(mg/l) determined by X-ray fluorescence
C021	120564	150	150	119
	120589	160	110	115
C022	120575	460	8	291
	120588	370	95	295
C023	120585	280	22	131
	120590	210	40	137
C038	120532	60	27	24
	120539	90	225	25
C046	120536	440	320	299
	120549	410	385	303
Relative average standard deviation (in percent)		14.7	52.6	1.56

7000 system amplifies and shapes detector-generated pulses that are proportional to incident X-ray energies. It digitizes these pulses, stores counts for each of these digitized energy values, and displays the acquired spectra on the video display in an intensity-versus-energy format. Lead peaks due to the irradiation of the sample chamber's lead shielding were present on most spectra obtained in the initial stages of method development. The peak heights were generally found to be inversely related to the solute concentration of the standards (fig. 3). In order to standardize lead-peak height regardless of solute concentration, an aluminum cap was placed over the samples and standards before they were rotated into analysis position over the Cd^{109} source. This removes from the spectrum the lead peaks produced by irradiation of the lead shield. Analyzing liquid rather than solid samples eliminates some possible sources of analytical error produced by variations in packing density, surface texture, particle size, and inhomogeneity of solid sample. However, there are still significant absorption and enhancement effects produced by co-existing solute elements on the analyte (the element concentration being determined) (Bertin, 1975) line intensity. Two methods that can be used to reduce or eliminate these absorption-enhancement effects are the standard addition method and the comparison-standard method. Both these methods were used and compared.

The comparison-standard method can significantly reduce absorption-enhancement effects if both standards and samples have a similar matrix (Bertin, 1975, p. 574). The standard addition or multiple standard addition method of analysis can eliminate matrix effects for elements that are not a large percentage of the total solute load. In the standard addition method, a known quantity of the analyte is added to the sample, and the analyte line intensity of both the sample and the sample with the standard addition are measured. Analyte concentration in the original sample is given by

$$Br_x = \frac{I_x V_s Br_s}{(I_x')\,(V_s + V_x) - I_x V_x}$$

where Br_x is the bromine concentration in the original sample; Br_s is the bromine concentration of the standard; and I_x and I_x' are the bromine Kα line intensities of the sample and the sample with standard added, respectively. V_x is the volume of the sample and V_s is the volume of the standard added. Multiple standard additions are used either if the intensity of the analyte line is not a linear function of the analyte concentration or in order to improve

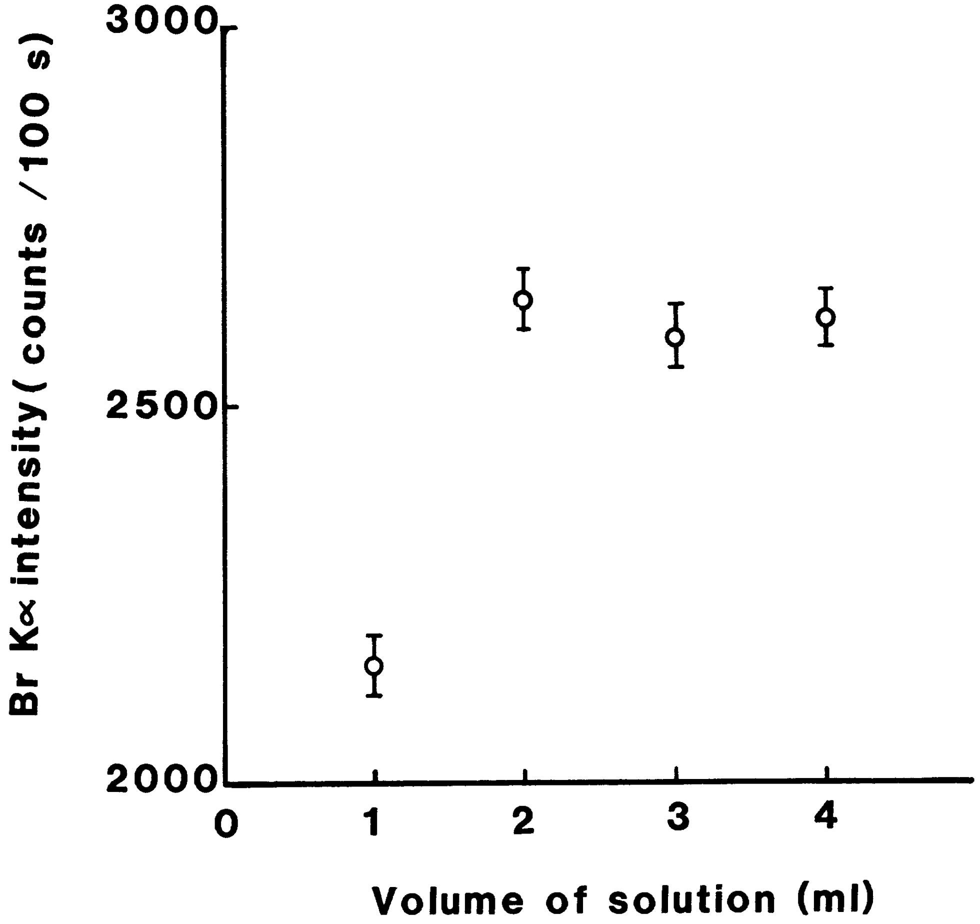

Figure 2.–Effect of the sample volume used for analysis on the intensity of the bromine Kα peak. The bars through each experimentally determined point indicate one standard deviation in the determination of that point.

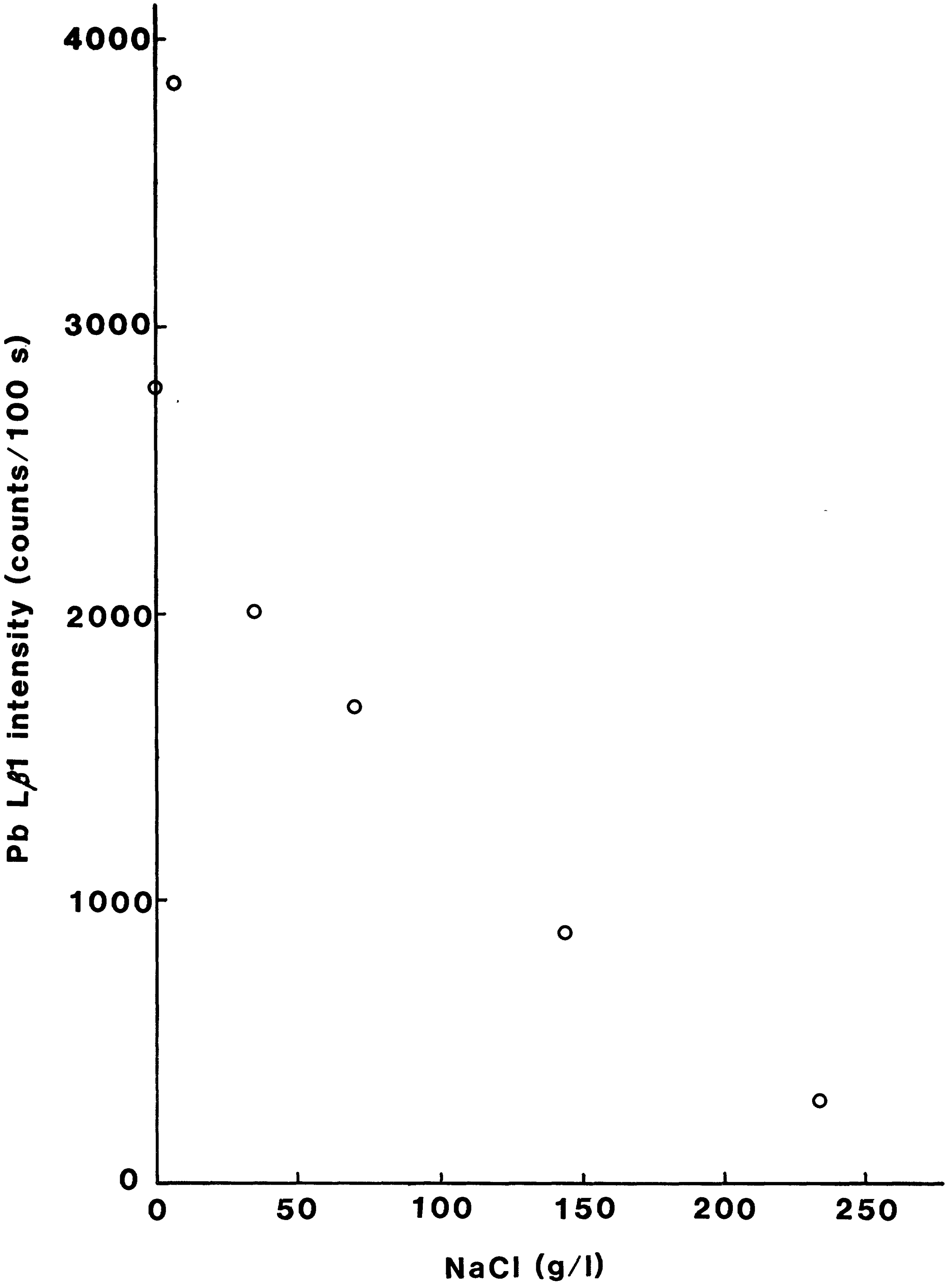

Figure 3.–Effect of NaCl concentration on the Pb Lβ1 peak intensity.

the precision of the determination. With multiple standard additions the concentration of bromine in the sample can be found using a graphical technique. If the amount of bromine added to the sample is the abscissa and the intensity of the bromine $K\alpha$ peak is the ordinate, then the intercept with the abscissa of the least-squares straight line that best fits the experimental points represents the absolute value of the concentration of bromine in the sample (fig. 4). As indicated by figure 4, the response of the bromine $K\alpha$ peak to increases in bromine concentration was linear over the concentration range considered; therefore, the multiple standard additions to the sample were made to improve the precision of the bromine determination.

While the standard addition method will eliminate absorption-enhancement effects, it is not suitable for large numbers of samples because each sample must be analyzed at least twice. A comparison-standard method is usually preferable for large numbers of samples because once the standard curve or curves are drawn it is unnecessary to obtain multiple analyses of the sample. However, unless the matrix of the standards closely matches that of the samples, absorption-enhancement effects cannot be reduced to an acceptable level. In the Eastern Province waters, sodium and chloride are the dominant ions (fig. 1) and a series of standards were made with $NaCl$ concentrations which varied from 0 to 234000 mg/l (fig. 5). The addition of $NaCl$ to the bromine standards clearly affects the bromine $K\alpha$ peak intensity. A sample usually does not contain equal amounts of sodium and chloride and the average $NaCl$ concentration, on a molar basis, of the previously analyzed sample was calculated and used when comparing it to the standard curves. Figure 6 indicates that the slope of the various bromine standard curves, when plotted against increasing $NaCl$ concentration, appears to decrease in a linear manner for $NaCl$ concentrations greater than or equal to 70000 mg/l. Extrapolation of this curve allows the slope of bromine standard curves, for samples whose $NaCl$ concentration is greater than 234000 mg/l, to be estimated. Because solubility of some other chloride-containing minerals is greater than that of $NaCl$, the average sodium plus chloride concentration of a few samples was higher than the standard with the highest $NaCl$ concentration (234000 mg/l).

In order to test the effect of ions other than sodium and chloride on the bromine $K\alpha$ peak intensity of field-collected water samples, 16 water samples from the Eastern Province of the Kingdom of Saudi Arabia were analyzed using both the multiple standard addition method and the standard-comparison method (table 2). The samples were chosen to cover a wide compositional range. The relative average standard deviation of 6.6 percent between the two methods

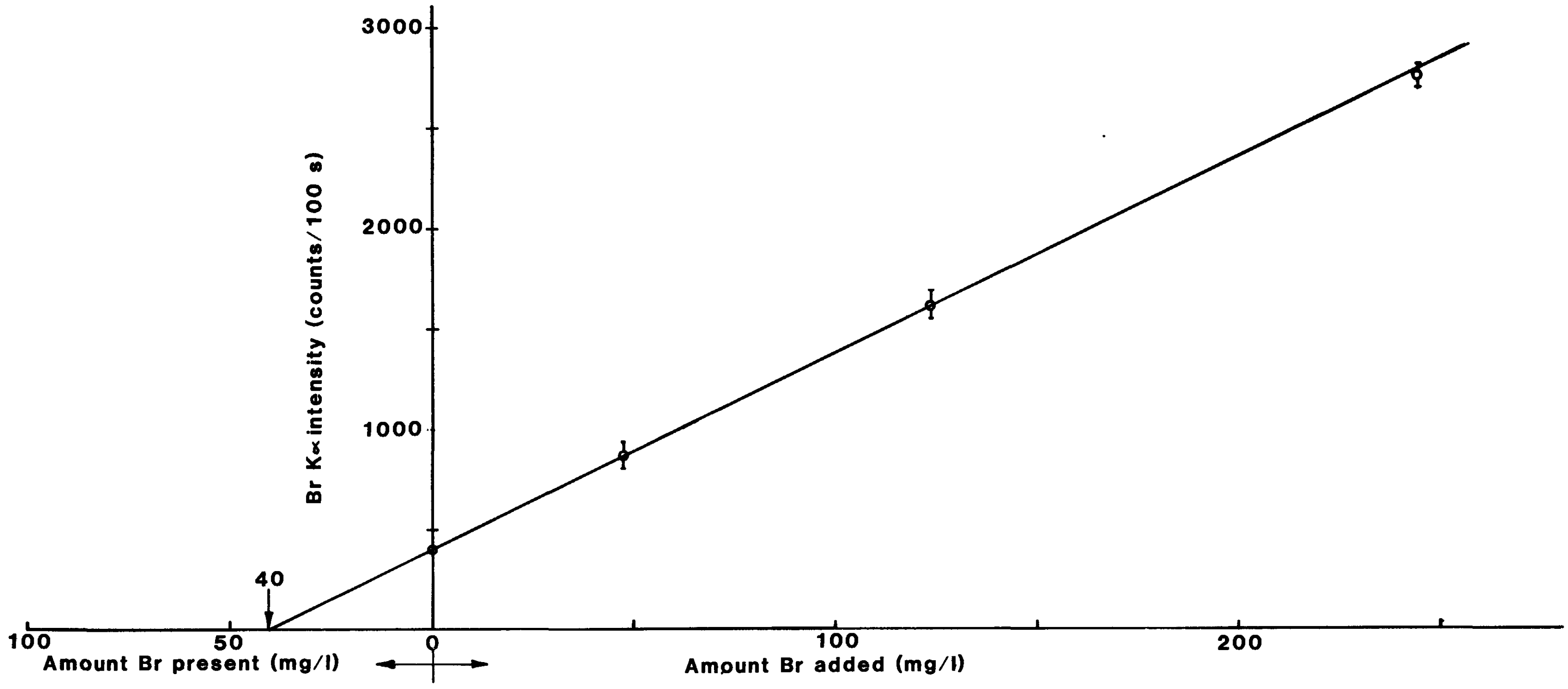

Figure 4.–An example of bromine determination using the method of multiple standard additions. The sample used is DGMR sample number 120520 and the correlation coefficient (r) is .9998. The bars through each experimentally determined point indicate one standard deviation in the determination of that point.

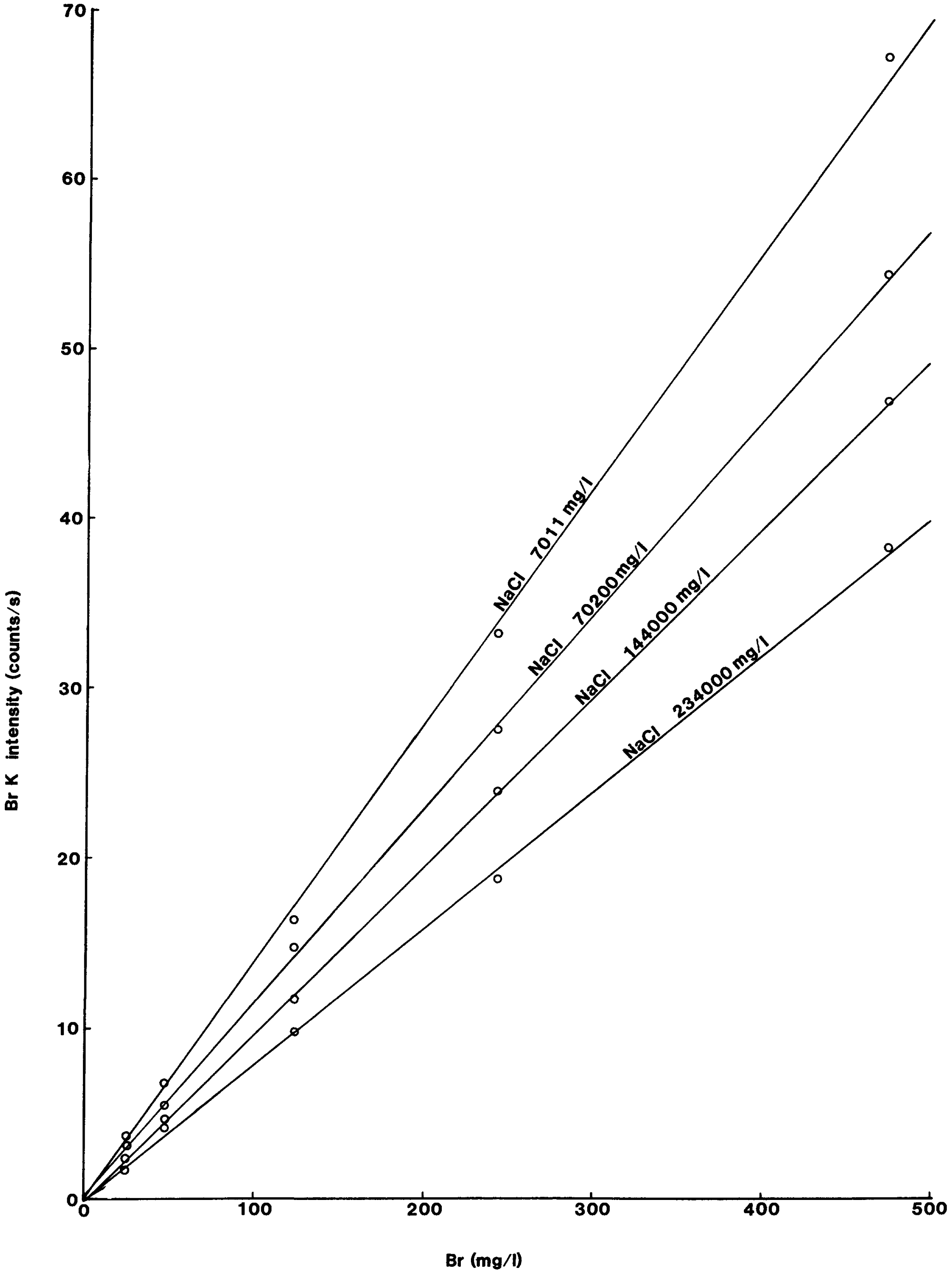

Figure 5.–Some experimentally determined linear least squares lines of the bromine standards. The number immediately above each line is the NaCl concentration of the matrix of the bromine standards which form that line.

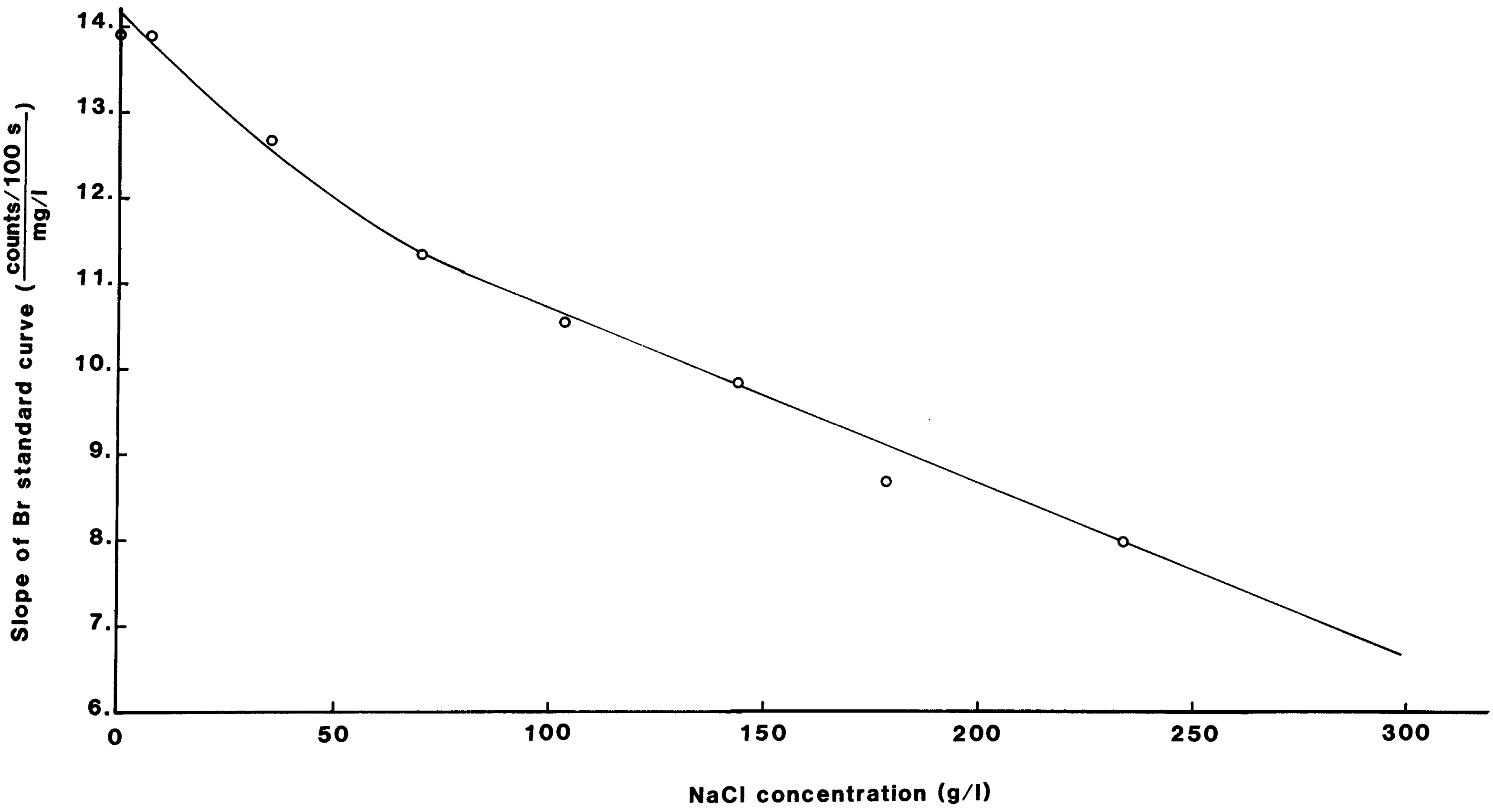

Figure 6.–Effect of NaCl concentration on the slope of the bromine standard lines.

Table 2.--*Comparison of bromine analytical results using the method of multiple standard additions and the standard-comparison method*

[The relative average standard deviation (Garrett, 1969) of the bromine concentration determined by the two methods is 6.6 percent]

DGMR sample number	Br(mg/l) determined by method of multiple standard additions	Br(mg/l) determined by standard comparison method
144043	87	89
144023	19	17
144004	39	36
120525	253	221
120576	347	351
120538	113	108
144005	30	28
144040	87	80
144002	15	13
120585	145	131
120575	290	291
120564	125	119
144001	15	15
120520	41	37
144009	20	23
144027	10	10

indicates NaCl dissolved in distilled water is a sufficiently close approximation to sample matrices. The correlation coefficients of the standard curves have values of .9996 or greater and support the indication that the response of the intensity of the bromine Kα peak to increasing concentrations of bromine is linear from about 5 to at least 476 mg/l.

The lower limit of detection for an element is defined as the analyte concentration equivalent to two times the standard deviation of the background. The background is determined by repetitive analysis of a blank. The lower limit of determination is defined as the concentration which gives a net signal equivalent to 10 times the standard deviation of the background (Winge and others, 1977). Limits of detection and determination were found for count times of 100 and 500 live seconds by 30 and 25 repetitive analyses of blank samples, respectively.

Table 3.--*Limits of detection and determination of the* X-*ray fluorescence method of bromine analysis*

	Br (mg/l) 2σ limit of detection	Br (mg/l) 10σ limit of determination
100 live-second count time	8.3	41.5
500 live-second count time	3.12	15.6

The limits of detection and determination are low enough that the bromine concentration of most of the water samples collected in the Eastern Province can be analyzed by the method presented in this paper with acceptable accuracy and precision.

SUMMARY

The energy dispersive X-ray fluorescence method presented in this paper is useful in the analysis of bromine in natural water regardless of chlorine concentration, provided the bromine concentration exceeds 15 mg/l. To a great extent, this restricts its use to brackish waters and brines where the concentration of bromine can be relatively high compared to fresh water. While the standard-comparison method has adequate precision for the brines from the Eastern Province where sodium and chloride are the dominant ions, samples with widely varying matrices from other areas might have absorption-enhancement effects that would have to be corrected using the method of standard addition. The method presented here has the advantages of being relatively quick to perform, requiring little sample preparation, and being suitable for use by semi-skilled technicians.

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