DETERMINATION OF DISSOLVED ALUMINUM IN WATER SAMPLES

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ABSTRACT

A technique has been modified for determination of a wide range of concentrations of dissolved aluminum (Al) in water and has been tested. In this technique, aluminum is complexed with 8-hydroxyquinoline at pH 8.3 to minimize interferences, then extracted with methyl isobutyl ketone (MIBK). The extract is analyzed colorimetrically at 395 nm. This technique is used to analyze two forms of monomeric Al, nonlabile (organic complexes) and labile (free Al, Al sulfate, fluoride and hydroxide complexes).

A detection limit 2 µg/L is possible with 25-ml samples and 10-ml extracts. The detection limit can be decreased by increasing the volume of the sample and (or) decreasing the volume of the methyl isobutyl ketone extract. The analytical uncertainity of this method is approximately ∓5 percent. The standard addition technique provides a recovery test for this technique and ensures precision in samples of low Al concentrations. The average percentage recovery of the added Al plus the amount originally present was 99 percent.

Data obtained from analyses of filtered standard solutions indicated that Al is absorbed on various types of filters. However, the relationship between Al concentrations and absorption remains linear. A test on standard solutions also indicated that Al is not absorbed on nitric acid-washed polyethylene and polypropylene bottle walls.

INTRODUCTION

The major problem encountered by many investigators in analyses of aluminum (Al) in natural water is to distinguish dissolved Al from particulate Al. Previously it was assumed that filtration of water samples through 0.45- µm filters removes all particulate matter from water. However, this assumption was shown to be incorrect (Hemn and others, 1973; Kennedy and others, 1974; and Barnes, 1975). It was found that filtration through filters with pore size as small as 0.1 µm does not remove all the particulate matter present in natural water samples (Barnes, 1975, and Stoffyn, 1979).

To overcome this problem, Stoffyn (1979) used two fluorimetric methods for determination of dissolved monomeric Al. Both methods, the Lumogallion (Shigematsu and others, 1970, and Hydes and Liss, 1976) and the Manganon (Dagnall and others, 1965) are based upon the formation of an organic chelate with Al. When excited to fluoresence at a given wavelength, the chelate emits a quantity of light proportional to Al concentration in the original sample. The detection limits of the Lumogallion and the Manganon methods for Al are 0.05 and 0.3 µg/L, respectively. Both methods have high sensitivity; however, fluoride, iron and organic matter contents of the water interfere with the accuracy and precision of Al determintion.

Another problem encountered by several workers in the determination of Al and other trace metal is absorption of the dissolved elements on the sampling container wall (Stoffyn, 1979). Acidification of the sample with Ultrex1/ nitric acid to pH <1.5 was found to eliminate this problem (Subramanian and others, 1978). However, acidification changes distribution of elemental species, which is not desirable, particularly in Al determination. Colloidal polymeric aluminum and strong alumino-organic complexes are acid soluble. Stoffyn (1979), p. 121-149, used Teflon bottles to reduce the absorption of dissolved Al on the sampling container walls. Barnes (1975), suggested extraction of Al immediately after collection if only dissolved equilibrium Al species are to be determined.

Driscoll (1980), p. 103-113, originally used the Ferron-orthophenanthroline colorimetric technique for Al determination. However, later he found that the methyl isobutyl ketone (MIBK) extract method, which was originally developed by Barnes (1975), is advantageous (Driscoll, oral communication, 1981). The method is based on chelating Al with 8-hydroxyquinoline (oxine) at pH 8.3, extracting Al-oxinate with MIBK and determining the Al in the extract by atomic absorption spectrophotometry (A.A.). The optium range of the MIBK extract technique is 2-50 µg/L for 400-mL samples, but the range may be extended for waters containing higher concentrations of Al by extracting from a smaller volume. Standards should be extracted from the same size aliquots as used for the sample (Barnes, 1975).

Aluminum reacts with 8-hydroxyquinoline in a pH range of 4.2-11.5 (Morrison and Freiser, 1957; and Sandell, 1959). A pH 8.3 was chosen as optimum to minimize interferences of calcium and magnesium at higher pH and fluoride at lower pH (Barnes, 1975). Iron (Fe) reacts with 8-hydroxyquinoline under the optinum conditions of this technique. Addition of hydroxylamine, hydrochloride, and phenanthroline - 1,10, reduces the Fe^{3+} to Fe^{2+}, and eliminates iron interference in the MIBK extract (Barnes, 1975).

May and others (1979) developed an extraction technique based on chelating Al with 8-hydroxyquinoline, then extracting with toluene. They measured the toluene extract colorimetrically at 395 nm. The detection limit of this technique is 0.2 µg/L for 100-mL samples. Preliminary extractions with chloroform solutions of diethylammonium diethyldithiocarbonate eliminate interferences due to dissolved V, Fe, Ni, Cu, Ga, Mo, and U.

1/ The mention of brand name does not constitute endorsement by U.S. Geological Survey.

Driscoll found that the color of the MIBK extract is stable and not time dependent as is the organic chelate used in the fluorometric method (Driscoll, oral communication, 1981). Accordingly, he determined the Al concentration colorimetrically at 395 nm. Because this method is sensitive only to dissolved Al, Driscoll did not filter the water samples thus eliminating the problem of Al absorption on filters. He also extracted the samples in the field to eliminate Al absorption on the sample bottle walls.

Three fractions of Al in natural water are measurable, nonlabile monomeric (monomeric alumino-organic complexes), labile monomeric (free Al, monomeric Al sulfate, fluoride and hydroxide complexes), and acid soluble (colloidal polymeric, strong organic complexes). Acid soluble Al is determined as the difference between total Al acid digested and total monomeric Al. Total monomeric Al are separated into nonlabile (cation-desalted) and labile fractions by passing the water sample through a column of strongly acidic cation-exchange resin (Amberlite-120). Driscoll (1980) found that the cation-desalted Al measurement is dependent on flow rate through the resin column. He suggested a constant high flow rate of 35 mL/min to minimize organic complex disruption by the resin. Driscoll (1980) used a Mariotte flask reservoir to maintain a constant operating pressure and to minimize variations in the flow rate.

The purpose of this report is to test the accuracy and precision of the MIBK extract technique and its suitability for Al determination in rain, surface waters, ground waters, and effluents obtained from leaching various types of rocks with acidified water. The present study investigates the accuracy, precision, and detection limit of this technique and reports methods for improvement. The purpose of the report also is to test the effect of filteration of water samples and the storage of samples in conventional polyethylene (CPE), linear polyethylene (LPE), and polypropyene (PP) bottles on accuracy of Al determination.

METHODS AND RESULTS

A modification of the MIBK extract technique as described by Barnes (1975) has been adopted. The volume of the samples and the standards are reduced to 25 mL instead of 400 mL used by Barnes. The volume of the reagents added are reduced concomitantly. Two drops of phenol-red indicator, and 0.5 mL of 5 percent 8-hydroxyquinoline are mixed with a 25 mL sample in a separatory funnel. Ten molar NH4OH is added, dropwise, while swirling until the solution turns red (pH ≈ 8), then 1-mL buffer solution with a pH of 8.3 (233 mL of 10 M NH_4OH and 115 mL of glacial acetic acid per liter) and 10 mL MIBK are added immediately.

The funnel is shaken vigorously for at least 10 seconds but no more than 30 seconds after which the phases are separated. The MIBK extract is collected. Aluminum concentration is determined colormetricly by measuring the absorbance of the MIBK extract at a wavelength of 395 nm.

Samples containing high concentrations of iron turn a greenish-black color or precipitate with the addition of 8-hydroxyquinoline. When this occurs, the sample is discarded and a new aliquot is treated to reduce the Fe^{3+} to Fe^{2+} before the extraction of Al. The treatment involves addition of 1 mL of 20 percent hydroxylamine hydrochloride and 1 mL of 1 percent phenanthroline - 1,10, adjustment of pH to 4, and a reaction time of at least 30 minutes.

To test the effect of various filters on Al concentrations, 4 sets of standards each containing 25, 50, 75, and 100 μg/L were filtered, then analyzed. The filters tested were 0.1-μm and 0.4-μm cellulose acetate, 0.45-μm Teflon and 0.45-μm silver. The results of the test (fig. 1) indicate that absorbance of Al does occur on all kinds of filters. However, the relationship between Al concentrations and absorbance remains linear. The least absorbance occurs on cellulose acetate filters.

An experiment was made to determine whether the use of Teflon bottles to collect water samples is necessary to reduce absorption of Al as suggested by Stoffyn (1979). Four sets of standards each containing 10, 25, 50, 75, 100, 200, and 500 μg/L prepared and stored for 14 days. One set was contained in Teflon bottles, the others were contained in CPE, LPE, and PP bottles. These bottles were presoaked in 50 percent nitric acid for at least 24 hours then rinsed thoroughly and soaked in deionized water for at least 48 hours. The deionized water was changed several times. Treatment with nitric acid is believed to saturate the absorption sites in polyethylene and polypropylene with nitrate. Klouda (1977), p. 50-52, used this method to clean bottles; however he used concentrated nitric acid.

The results of that test indicate that no Al adsorption occurs on nitric acid washed CPE, LPE, and PP bottle walls. The results in figure 2 indicate that the optimum range of the MIBK extract technique may be extended to 1,500 μg/L if the volume of the sample is reduced to 25 mL.

In order to determine the suitability and precision of the MIBK extract technique for Al determination in various types of water of interest to us, rain water, surface water, and spring water from watersheds developed on various bedrock were collected and analyzed. Effluents obtained from leaching sandstone and granite with acidified water of pH 2 and 5 were analyzed. Samples were prepared and analyzed in triplicate, to determine the precision of the technique.

Of major interest is the determination of total monomeric Al. Separation of the nonlabile fraction of monometric Al in natural water was also tested. Amberlite-120 was used to separate both forms of monomeric Al. The method used is based on the method described by Driscoll (1980). A flow rate of approximately 35 mL/min was used. A constant flow was maintained using a constant operating pressure and control valves (Fig. 3). After the cation-desalted sample (nonlabile) is collected, 100 mL of sodium chloride solution eluent was passed through the resin prior to introduction of the next sample. Total Al (monomeric and colloidal) was also measured using the flameless atomic absorption technique. Injection of samples into the combustion furnace was done by an automatic sampler to reduce the effect of manual injection on the reproducibility of the results.

It was found that 25 mL is a suitable sample volume for Al^{3+} determination in most surface and ground water. However, some of the effluents obtained from the leaching experiment needed dilution. The volume of rain samples usually has to be at least 100 mL. However, using the standard addition technique and reducing the volume of the MIBK extract to 5 mL, it was possible to determine monomeric Al in 25-mL rain samples (fig. 4).

The results of the analyses (Table 1) indicate that differences in the concentrations of Al in the triplicate extractions of natural samples are about ±5 percent. However, the difference is higher in some of the samples from the leaching experiments because of the analytical error resulting from dilution. To test the accuracy of the MIBK extract technique, recovery tests were done on the natural samples collected. Known amounts of Al, ranging in concentrations between 5 and 20 µg/L were added to aliquots of the natural samples, then the total Al was extracted. The average recovery of the added Al plus the amount originally present was 99 percent (table 2).

CONCLUSIONS

The MIBK extract technique is an interference-free technique and is suitable for determination of dissolved Al in various types of water without using further purification techniques as those employed by May and others (1979). The detection limit of this technique, if Al is determined colorimetrically, is 2 µg/L for 25-mL samples and 10-mL MIBK extracts. However, lower detection limits can be achieved by increasing the volume of the sample and (or) decreasing the volume of the MIBK extract. The analytical uncertainity of the method is ±5 percent and the recovery of the added Al is 99 percent. Application of the standard addition technique to this method ensures the precision of determination of low Al concentration.

Cellulose acetate filters were the least adsorbant, among those tested for Al. To eliminate the error due to adsorption on filters, it is suggested that the standards be filtered with the same type of filters as the samples. It is not necessary to use Teflon bottles to store water samples for Al determination for short period of times. Polyetheylene and polypropylene bottles are satisfactory, if presoaked in 50 percent nitric acid then rinsed thoroughly and soaked in distilled water.

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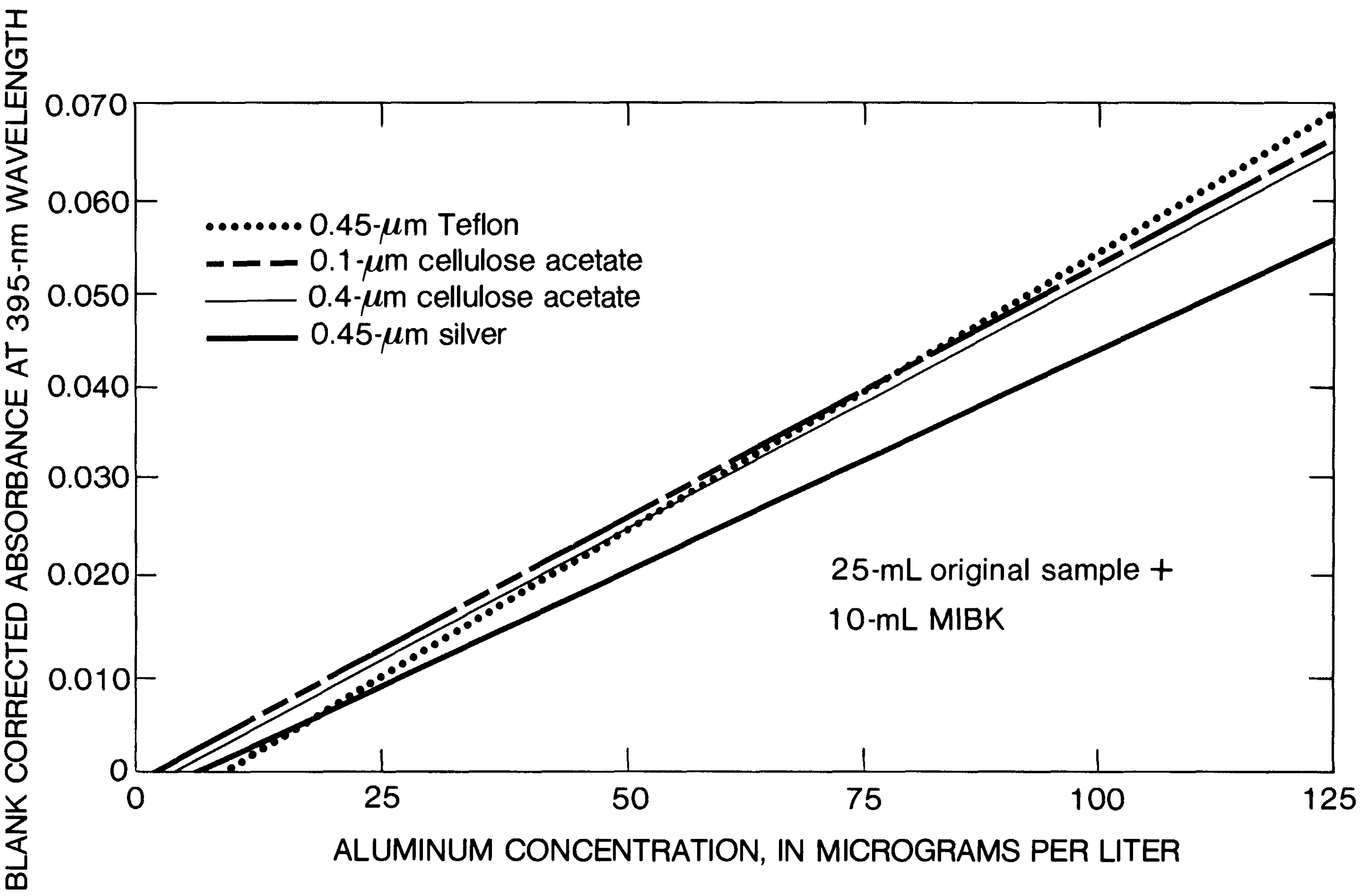

Figure 1.-- Effect of different filters on aluminum concentration in prepared standard solutions. MIBK is methyl isobutyl ketone.

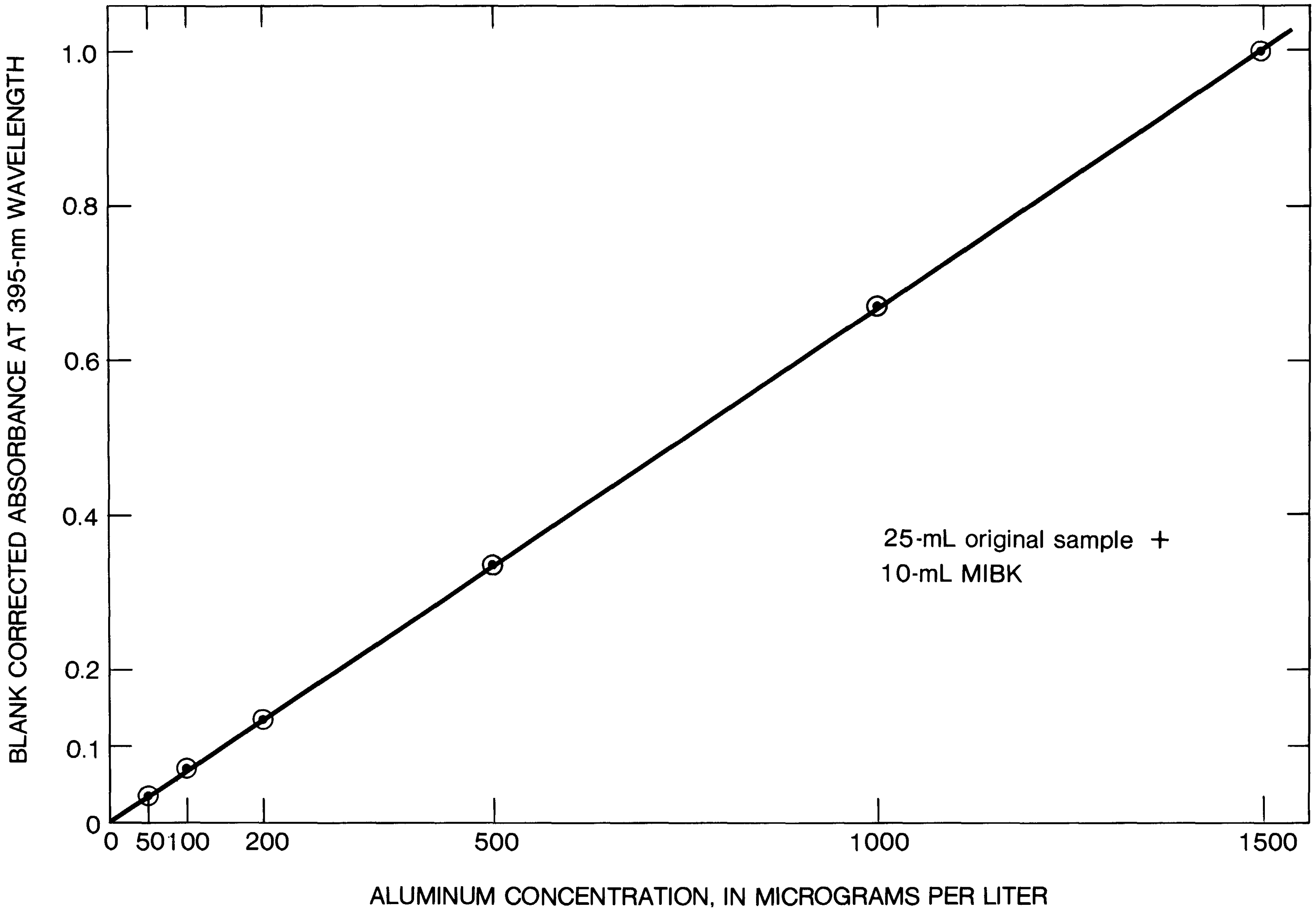

Figure 2.-- Optimum range of the methyl isobutyl ketone (MIBK) extract technique.

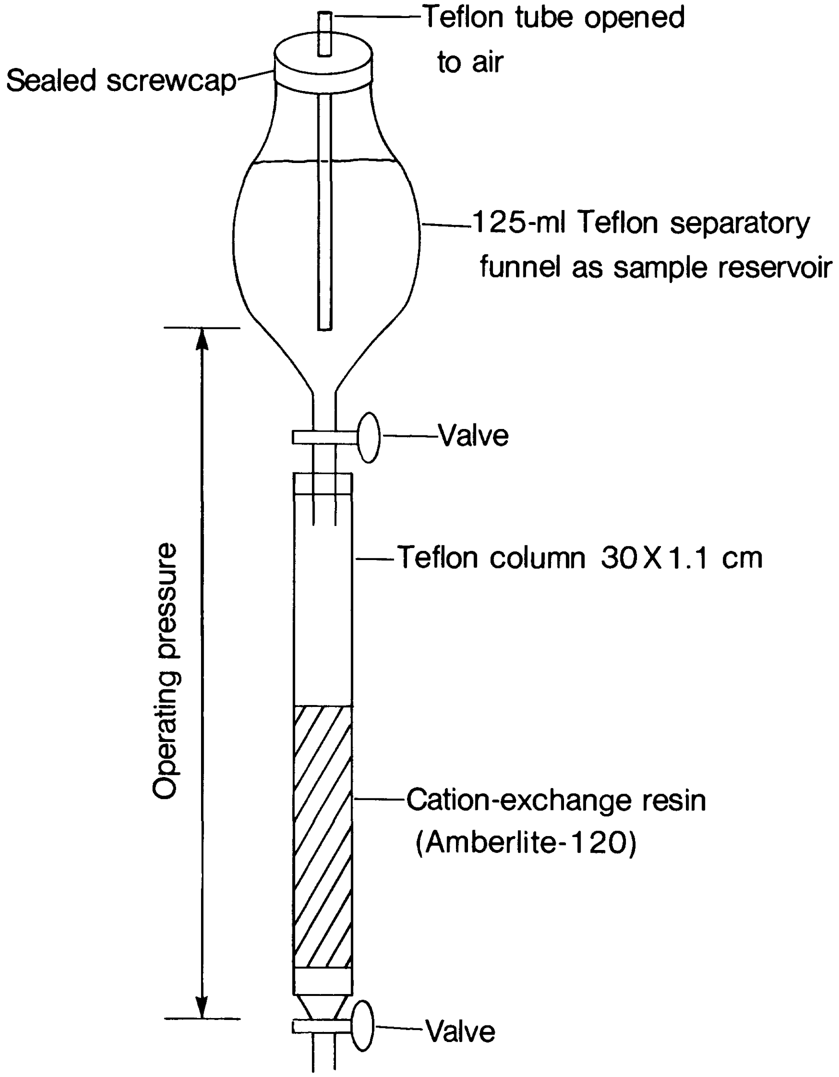

Figure 3.-- Sketch showing cation-desalting column (not to scale) for separation of nonlabile aluminum (monomeric alumino-organic complexes).

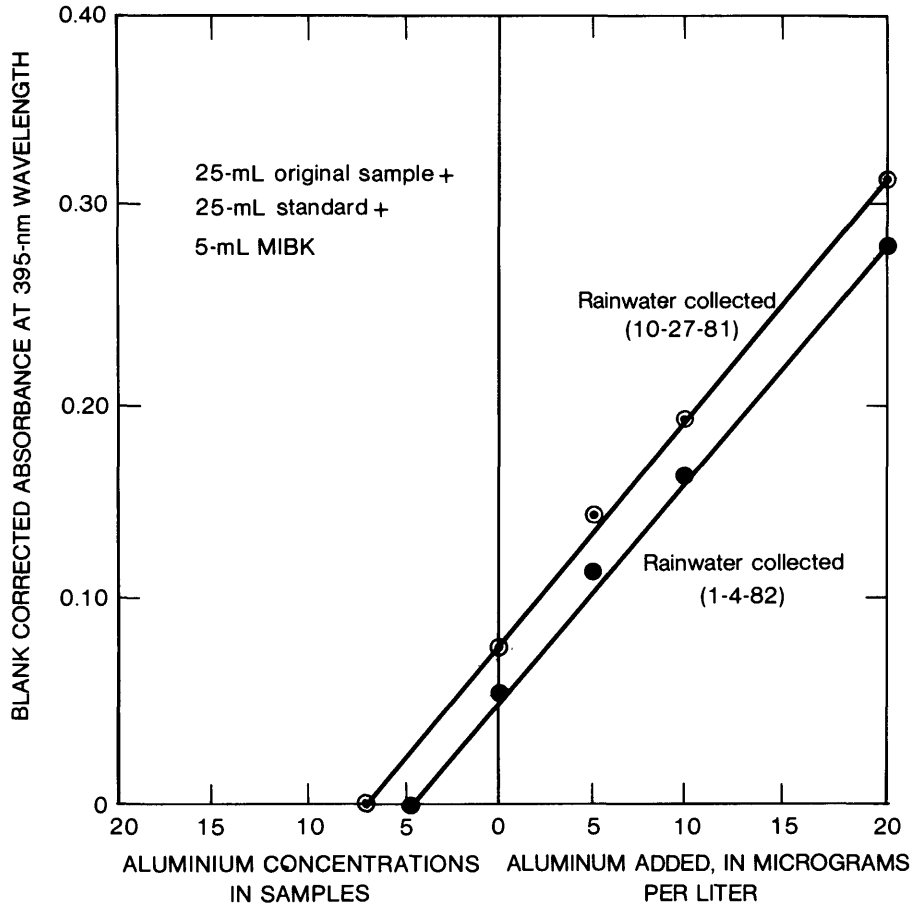

Figure 4.-- Example of analysis of rainwater by methyl isobutyl ketone (MIBK) extraction using the standard addition technique.

Table 1. Results of analyses for aluminum in different types of water

		Concentration in micrograms per liter			
Sample type	pH of sample	Monomeric non-labile Al	Monomeric labile Al	Total monomeric[1]/ Al ∓ 1 σ	Precision in percentage
Rain	4.9	n.d.	n.d.	7± 0.5	7
Rain	4.7	n.d.	n.d.	5± 0.3	6
Surface Water					
Watershed developed on sandstone					
downstream	5.88	123	97	220±6	3
upstream	4.8	122	161	283±5	2
Watershed developed on shale					
downstream	7.26	n.d.	n.d.	33±2	6
upstream	5.21	48	35	83±3	4
Watershed developed on granite					
downstream	6.68	n.d.	n.d.	30±2	7
upstream	6.74	n.d.	n.d.	25±1	4
Groundwater					
Spring in sandstone	6.05	n.d.	n.d.	55±2	4
Soil Water					
Soil developed on sandstone	6.15	n.d.	n.d.	75±2	3
Effluents obtained after 20 hours of leaching rocks with acidified water					
sandstone, pH 5	6.10	n.d.	n.d.	75±3	4
sandstone, pH 2	2.15	n.d.	n.d.	1,200±100	8
granite, pH 5	6.55	n.d.	n.d.	300±9	3
granite, pH 2	3.83	n.d.	n.d.	75,000±8,000	11

n.d. = not determined.

1/ The average of analyses of 3 different aliquots of the same sample.

Table 2.-Results of analyses for aluminum in natural water samples before and after addition of aluminum standard

Source of Sample	pH of Sample	Original concentration of aluminum[1]	Total recovered Aluminum[2]		
Rain	4.9	7	13 (108)	17 (100)	28 (104)
Rain	4.7	5	10.5 (105)	14 (93)	25 (100)
<u>Surface Water</u> Watershed developed on sandstone					
Downstream	5.88	220	220 (98)	219 (95)	235 (98)
Upstream	4.8	283	275	280	288
Watershed developed on shale	n.d.	n.d.	n.d. (95)	n.d. (96)	n.d. (95)
Downstream	7.26	33	37 (97)	41 (95)	51 (96)
Upstream	5.21	83	85 (n.d.)	90 (n.d.)	100 (n.d.)
Watershed developed on granite			(97)	(97)	(97)
Downstream	6.68	30	36 (n.d.)	42 (n.d.)	49 (n.d.)
Upstream	6.74	25	31 (103)	37 (106)	46 (102)

Average percentage of Al recovered was 99.29

n.d. = not determined

1/The average of analyses of 3 different aliquots of the same sample.

2/Upper value is Aluminum concentration in micrograms per liter. Lower value in parentheses is proportion recovered in percentage after addition of aluminum standard of 5, 10, 20, micrograms per liter.