

DETERMINATION OF COPPER IN SALINE WATERS BY ATOMIC ABSORPTION, SPECTROPHOTOMETRY COMBINED WITH APDC-MIBK EXTRACTION*

R. R. BROOKS, B. J. PRESLEY AND I. R. KAPLAN

Department of Geology, Institute of Geophysics and Planetary Physics, University of California, Los Angeles, Calif. (U.S.A.)

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RILEY¹ has summarized the available data for the determination of copper in sea water and has concluded that much of the early classical work is unreliable because of faulty analytical techniques and contamination. At present, atomic absorption spectrophotometry and neutron activation analysis would appear to offer the best promise for the determination of trace elements in sea water. Although many of these elements exist in sea water at concentrations below their detection limits by atomic absorption techniques, they can often readily be concentrated by extraction into a suitable solvent with an increase in sensitivity which is due not only to a favorable aqueous phase/solvent ratio but also to the existence of the "solvent effect"² which results in enhanced sensitivity. Clearly, a combination of solvent extraction and atomic absorption spectrophotometry should be useful for the determination of trace elements in saline waters particularly as it is often possible to insure that the alkali metals and alkaline earths are not simultaneously extracted. Direct aspiration of sea water usually results in difficulties associated with clogging of the burner and scattering effects because of the high solid content.

It is well known that ammonium pyrrolidine dithiocarbamate (APDC) is a useful chelating agent for a number of transition metals and furthermore will extract over a very wide pH range^{3,4}. Recently, SPRAGUE AND SLAVIN⁵ have shown that it may be used with methyl isobutyl ketone (MIBK) to separate trace elements from 25% potassium chloride solutions and have suggested its use for sea water. MAGEE AND RAHAMAN⁶ have used the system APDC ethyl acetate to determine copper in sea water. Ethyl acetate is, however, not a good solvent to use because of its appreciable solubility (9%) in water and because it shows a relatively poor solvent effect². MOLFORD⁷ has recently reviewed solvent extraction systems for use with atomic absorption spectrophotometry and has pointed out the advantages of the APDC-MIBK system.

The following work was carried out in order to investigate further the potentialities of the APDC-MIBK system and to apply it to the analysis of copper and other elements in sea water, interstitial waters of ocean sediments and other saline waters.

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EXPERIMENTAL

Apparatus

Atomic absorption measurements were carried out on a Perkin Elmer 303 Atomic Absorption Spectrophotometer equipped with a conventional burner for use with air-acetylene. The output of the instrument was connected to a Sargent Model MR Recorder via a Perkin Elmer Recorder Readout Accessory.

Reagents

Redistilled commercial-grade methyl isobutyl ketone, ammonium pyrrolidine dithiocarbamate supplied by Eastman Organic Chemicals and reagent-grade hydrochloric acid. The latter two reagents were sufficiently free of copper to render purification unnecessary. A standard copper solution containing 200 p.p.m. in distilled water was used and was diluted as required to give a solution containing 0.4 p.p.m. This latter solution was used immediately after preparation.

The distribution coefficient of copper between sea water and MIBK

When large sea water/solvent ratios are used, the percentage extraction of the copper will decrease as this ratio increases since the relationship between the distribution coefficient (D), the percentage extraction (E) and the volume of the organic phase (V_o) and aqueous phase (V_a) is given by the expression:

$$E = \frac{100D}{D + V_o/V_a}$$

Neglect of this relationship can often lead to significant errors in this type of work and the technique which has been developed, is designed to correct for incomplete extraction whatever its magnitude. The distribution coefficient for copper was determined by successive extraction of an aqueous solution containing 5 p.p.m. of copper at a pH of 3.0. Provided that extraction is reasonably complete, the ratio of the amounts in the two extracts is an approximate measure of D . A value of 620 was obtained for the distribution coefficient which corresponds to 95.0% extraction for a 15:500 solvent/water ratio.

The stability of the copper complex

The stability of the copper complex was tested by making an extract of the APDC complex into MIBK. This extract was divided into 3 portions, one of which was kept at room temperature and its absorbance measured at regular intervals. Another fraction was kept frozen in liquid nitrogen and thawed temporarily for absorbance measurements. The third portion was frozen in liquid nitrogen and warmed slightly until only the solvent had melted. A small amount of water remained in the vessel as ice and the solvent was removed by decantation. The absorbance of each sample was compared with that of a stable copper solution prepared from a mixture of hydrochloric acid, MIBK and acetic acid.

In all cases there was no appreciable lessening of the absorbance of the copper complex over a period of 8 h. This was in marked contrast to the stability of complexes of other elements which were examined simultaneously. For example, the stability of the manganese complex was greater in the frozen and dehydrated samples than in the "wet" portion maintained at room temperature.

The rate of uptake of copper

Samples of sea water containing added copper were extracted for varying periods and it was determined that a period of 10 min was necessary to insure that the copper extraction had reached its maximum.

The determination of copper in sea water and natural waters

The following technique was developed to compensate for any incomplete extraction of copper with high sea water/solvent ratios. The technique also allowed for simultaneous determination of both "soluble" and particulate copper.

Samples (500 ml) of freshly collected sea water which had been stored in polythene bottles, were filtered through a $0.45\text{-}\mu$ membrane filter. The filtrate contained the "soluble" copper. The millipore filters were dissolved in 1 ml of concentrated hydrochloric acid and 25 ml of MIBK. On gentle warming, complete dissolution was achieved and no further treatment was required. A blank was carried out simultaneously.

The pH of the filtrate was adjusted to 3.0 by addition of 2 *N* hydrochloric acid and the samples were placed in 1-l Erlenmeyer flasks. MIBK (25 ml) was then added to each flask followed by 5 ml of an aqueous 1% solution of APDC. At equilibrium, 10 ml of solvent entered the aqueous phase owing to its solubility. This resulted in a 15:510 phase ratio. The samples were then shaken for 10 min on an automatic shaker and the phases were separated via a separatory funnel. Clean separations were easily achieved and since concentrations only were involved, there was no need for a quantitative recovery of the solvent.

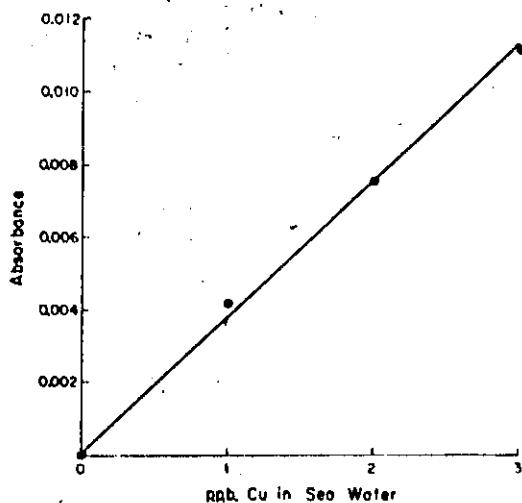


Fig. 1. Working curve for copper in sea water.

In order to prepare the working curve, the extracted sea water samples were combined and reextracted to insure that they were free of copper. Aliquots (500 ml) were then placed in clean Erlenmeyer flasks and sufficient copper was added from the freshly-prepared 0.4-p.p.m. solution to give concentrations of 0, 1, 2, and 3 p.p.b. in the sea water. MIBK (15 ml) and 5 ml of the APDC solution were then added, and shaking and phase separation were carried out as before. It will be noted that 15 ml

of solvent were used for the standards instead of 25 ml. This is because the sea water used for the standards had already been equilibrated with MIBK. A typical working curve is shown in Fig. 1.

The zero of the working curve was not satisfactory as a blank since it did not include the acid added to adjust the pH of the sea water or the amount of copper impurity in the 10 ml of solvent represented by the different amounts used for the samples and standards. The blank was carried out as follows. Sufficient hydrochloric acid corresponding to the amounts needed to adjust the pH of 10 samples was taken almost to dryness in a teflon beaker heated by an infrared lamp. MIBK (250 ml) was then added to the residue and heated until its volume had decreased to 150 ml. Fifteen ml of this "prepared" solvent was then added to a 500-ml quantity of twice-extracted sea water. This was followed by addition of 5 ml of APDC solution, equilibration for 10 min and phase separation.

All samples including the particulate specimens were then aspirated into a lean air acetylene flame. A $\times 10$ scale expansion and noise suppression 3 were used. The hollow cathode was a conventional Perkin Elmer lamp run at 15 mA for the analysis line at 3247 Å.

The oxidation state of copper in sea water

The experiments were carried out with copper(II). In case the existence of copper(I) in sea water could have affected the results, one of two identical samples of sea water was treated with a small quantity of bromine water to insure that all copper was in the divalent state. When this sample and the untreated sample were extracted in the normal manner, no noticeable difference in absorption was noted. There is therefore no need to oxidize sea water before these determinations of copper.

The precision of the method

The precision of the method was tested by carrying out determinations on 16 identical samples of sea water. The coefficient of variation was $\pm 10\%$. Considering the fact that this was for a copper content of around 1 p.p.b., this degree of precision must be considered satisfactory.

RESULTS AND DISCUSSION

Copper determinations were carried out on a number of sea water samples, interstitial waters and samples (3.6% solids) from the Salton Sea of California. The sea water samples were all taken from surface waters off the coast of S. California. The results are presented in Table I. All duplicates agreed well within experimental error. Three of the samples were repeated in duplicate at a later date and gave good agreement with earlier values. These are shown in parentheses in the Table. Where copper values were high, as in the Red Sea sample, phase ratios closer to unity were used to insure that values fell within the range of the working curve.

The sea water values are at the lower end of the suggested range of 1-20 p.p.b.¹ This may be due to the fact that they were taken off the coast of S. California at the end of the dry season when there is little runoff from the land. The average of 0.9 p.p.b. compares with a value of 1.85 p.p.b. obtained by other workers for

TABLE I

COPPER IN NATURAL WATERS

(All results in p.p.b.)

Type of water	Location	Lat.	Long.	Dissol. copper	Particulate copper
Sea water	Santa Barbara Basin	34° 13'	120° 02'W	1.33(1.49)	< 0.10
Sea water	Santa Cruz Basin	33° 42'	119° 36'W	0.85	0.34
Sea water	Continental Rise	33° 34'	120° 41'W	0.64(0.74)	< 0.10
Sea water	Tanner Basin	32° 57'	119° 45'W	0.60(0.57)	< 0.10
Sea water	Catalina Basin	33° 23'	118° 48'W	0.78	< 0.10
Lake water	Salton Sea	33° 20'	115° 47'W	1.33	0.25
Lake water	Salton Sea	33° 39'	115° 50'W	1.73	0.10
Marine marsh	Newport, California	33° 48'	117° 54'W	4.58	
Interstitial	Ocean sediment	33° 40'	118° 32'W	2.68	
Interstitial	Ocean sediment (Red Sea, Atlantis Deep)	21° 20'	38° 3'E	107.0	

Belfast Lough. There was little or no particulate copper except in the region of the Santa Cruz Basin.

The sensitivity of the method appears to be about 0.1 p.p.b. and is comparable to that of neutron activation which would be about 3 p.p.b. for raw sea water or about 0.1 p.p.b. for analyses on the solid matter. The method also appears to have the dual advantages of speed and adequate precision.

It is concluded that a particular advantage of the method lies in the self-compensation afforded by preparing a working curve by adding and extracting fixed amounts of copper to and from sea water. In this way, incomplete extraction of copper from the samples is corrected for. For this reason also, it has not been necessary to carry out the usual addition and recovery tests which are conventionally applied to a new technique.

Preliminary work has indicated that the copper extracts will probably be suitable for simultaneous determinations of nickel, cobalt, iron and possible manganese. It is hoped to apply the combined technique to the analysis of further samples of saline waters.

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SUMMARY

A technique has been developed for the determination of copper in saline waters by extraction of its complex with ammonium pyrrolidine dithiocarbamate into methyl isobutyl ketone and subsequent analysis by atomic absorption spectrophotometry. The method is self-compensating for any incomplete extraction of

copper. With a 15:510 solvent-aqueous phase ratio, a sensitivity of 0.2 p.p.b. and a precision of $\pm 10\%$ were achieved. The method was used to determine copper in a number of sea water and other saline water samples.

RÉSUMÉ

On a développé une méthode pour le dosage du cuivre en eaux salines. On a extrait le complexe avec du pyrrolidine-dithiocarbamate d'ammonium en solution de méthylisobutylcétone et effectué la détermination finale par spectrophotométrie par absorption atomique. La méthode possède une compensation interne pour l'extraction incomplète du cuivre. La précision obtenue est de $\pm 10\%$ et la sensibilité est d'environ 0.2 p.p.b. On a utilisé la méthode pour le dosage du cuivre dans l'eau de mer et autres échantillons salins.

ZUSAMMENFASSUNG

Ein Verfahren wurde für die Bestimmung von Kupfer in salzhaltigen Wassern entwickelt. Es bestand aus der Extraktion des Komplexes mit Ammoniumpyrrolidindithiocarbamat im Methylisobutylketon mit anschließender Bestimmung mit Flammenabsorptionsspektroskopie. Das Verfahren enthält Selbstkompensation für unvollständige Kupferextraktion. Eine Genauigkeit von $\pm 10\%$ und eine Empfindlichkeit von etwa $2 \cdot 10^{-8}\%$ wurde erreicht. Die Methode wurde verwendet um Kupfer in verschiedenen Seewasser- und Naturwasserproben zu bestimmen.

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