

A CHELATION–SOLVENT EXTRACTION-BASED METHOD FOR THE ESTIMATION OF LEAD AND CADMIUM IN DRINKING WATERS BY THE ATOMIC ABSORPTION TECHNIQUE

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الخلاصة :

تم استعمال طريقة التركيز مسبقاً في وسط حامضي بوسيلة الاستخلاص بالمذيبات ، وذلك باستخدام مركب (امونيوم بايروليدين دايثيوكاربوميت) لتقدير كل من الرصاص والكاديوم في مياه الشرب بأسلوب الامتصاص الذري .
لقد وُجد أنه في ظروف تشغيلية مثلى بخصوص معدل سريان الوقود مع الهواء ، وارتفاع المُحرِّق ، وتيار المصباح فقد تم دراسة حساسيات الامتصاص كدالة الحامضية الوسط ، وبالمحافظة على حامضية مثلى للمحلول تتراوح بين ٢,٥ إلى ٣,١ باستخدام حامض الخليك الجليدي ، أمكن استرجاع ٨٠٪ من هذين الفلزين بخطوة واحدة .
ولقد تم حساب العناصر المعرزة لسته مذيبات عضوية بمعدل دقة مقداره ١,٥٪ بنسبة س/ن عالية نوعاً ما .
إن هذه الطريقة كمية . ويستخدم فيها ١٥ سم^٣ فقط من عينة الماء المعدة للتحليل ، ويمكن استخدامها لتعيين العناصر الشحيحة في مياه متعددة الصفات . وكان الحد الأدنى من تقدير كمية العناصر في مياه الشرب هو حوالي ٠,٠٢ ميكروغرام / لتر بالنسبة للكاديوم و ٠,٤٠ ميكروغرام / لتر للرصاص .

ABSTRACT

An acid-medium ammonium pyrrolidine dithiocarbamate (APDC) based chelation–solvent extraction preconcentration method is proposed for the estimation of lead and cadmium in drinking waters by the atomic absorption technique. Under optimized operating conditions in terms of fuel/air flow rates, burner height, and lamp current, the absorption sensitivities are studied as a function of pH of the medium. An optimal pH range of 2.5–3.1, maintained with glacial acetic acid, gives above 80 percent recovery in a single-step extraction of these metals. Enhancement factors are computed for six organic solvents with an average precision of $\pm 1.5\%$ at a fairly high S/N ratio. The method is quantitative, employs only a 15.0 ml aliquot of the water sample to be analyzed, and has the potential of application to trace metal estimation in waters of varied nature. The lower detection limit achieved is 0.02 $\mu\text{g/l}$ for cadmium and 0.40 $\mu\text{g/l}$ for lead.

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INTRODUCTION

Many inorganic pollutants are present in drinking waters in trace amounts; analytical methods of improved sensitivity and detection limits are therefore needed for their estimation. Specifically such improvements have been sought for the atomic absorption spectrophotometric (AAS) method as applied to the estimation of trace metal levels in various types of waters. Recognition of the role of non-essential trace metals and of their adverse impact on human health has made precise understanding of the extent and mode of pollution arising from specific metal pollutants essential. In view of the known health hazards associated with the intake of lead and cadmium from drinking waters, more rigorous attention is now being paid to the detection and estimation of these trace metals through analytic procedures of high precision and sensitivity. Of the several physical and chemical methods available for this purpose, chelation followed by solvent extraction constitutes the single most useful method for the estimation of trace metals in waters. Excellent texts and reviews are available to this effect [1-3]. A comprehensive review on the application of chelate complexes to flame atomic absorption technique has been given by Robinson [4]. Sperling [5] and Fujiwara et al. [6] have described an ammonium pyrrolidine dithiocarbamate (APDC) based preconcentration technique for cadmium in water prior to determination by flame atomic absorption spectrometry. Brueggemeyer and Caruso [7] have described a new method for the determination of lead, whereby it is extracted as the dithiocarbamate into chloroform with a 6.8% relative standard deviation at the 50 $\mu\text{g/l}$ level. Many other workers have reported high sensitivity solvent extraction procedures for the estimation of these metals in waters of varied nature [8, 9]. Basically, the chelation extraction systems involve the complexation of trace metals by reagents satisfying simultaneously the charge neutralization and coordination number requirements, thus yielding compounds much more soluble, at specific pH ranges, in inert organic solvents than in water [10]. APDC has been used most successfully for trace metal preconcentration purposes in conjunction with methyl isobutyl ketone (MIBK) as the extracting solvent, at specific pH

ranges for various trace metals [11]. The chief advantages of the APDC chelation solvent extraction method include simplicity, speed, high specificity, and direct application. In addition, the method not only enhances the absorption sensitivity and the limit of detection, but also serves to separate and/or concentrate other metal ions present in a given water sample.

With the above cited objectives in view, use is made of APDC in the present investigation for the estimation of lead and cadmium in drinking waters. Optimum absorption conditions are established for each of these metals separately at sufficient flame stability to yield high accuracy and precision. In order to study the role of solubility in a given solvent in the enhancement of absorption sensitivity, the optimization of such conditions as fuel flow rate, oxidant flow rate, burner height, and lamp current, together with pH of the medium, is a prerequisite. The optimum pH range is obtained using glacial acetic acid. The method does not employ any conventional buffers. The procedure involved utilizes only 15.0 ml of the water sample to be analyzed with 10.0 ml of the solvent used in a single-step extraction, as against large sample aliquots (~100-200 ml) required in conventional multistep separations recommending batchwise use of solvents for metal extractions [12]. The method has the potential of application to the estimation of trace metals other than lead and cadmium in surface, underground, or raw spring waters.

EXPERIMENTAL

All absorption measurements were made with a Hitachi Atomic Absorption Spectrophotometer. Doubly distilled water was used both for aspiration and for preparation of standard solutions. All reagents used were of Research Grade. Solvents used were at least 99.5% pure. Stock concentrations of cadmium and lead standards were 100 mg/l in the metal ion. Appropriate aliquots were taken from these standards and diluted to the desired concentration level.

The experimental procedure involved in taking a precisely measured 15.0 ml aliquot of the water sample in a prewashed, dried pyrex beaker (50 ml capacity), adjusting the pH of the medium by the

addition of 1–2 ml of glacial acetic acid ($d=1.06$ g/ml) to the desired value, and adding 1.0 ml of 2.0% freshly prepared aqueous APDC solution to it. Then, 10.0 ml of the relevant organic solvent was added and the mixture was shaken gently for 5 minutes and allowed to stand for 10 minutes in a test tube placed in a rack. Thereafter, the organic phase was separated. In cases where the organic phase formed the upper layer, direct aspiration was conducted. An identical procedure for the extraction and aspiration of standards and blanks was followed.

Optimum absorption conditions were established for each extracted organic phase in terms of pH of medium, air flow rate, fuel flow rate, burner height, and lamp current. The reproducibility of the method was checked by absorption measurements on repeated runs. In order to quantify the extractions, aqueous/organic phase aspirations were effected with variable volumes of the extracting solvents. Various locally available drinking waters were used in this study.

DISCUSSION

The data on the optimization parameters for various solvent systems appear in Table 1. It is found that the absorption signals of lead and cadmium in various solvents are highly pH-dependent, as shown

in Figure 1. The role of fuel and air flow rates is also critical. For instance, the cadmium–acetophenone system gives optimum sensitivity at a fuel rate of 0.7 l/min and air flow rate of 6.7 l/min at pH 2.8.

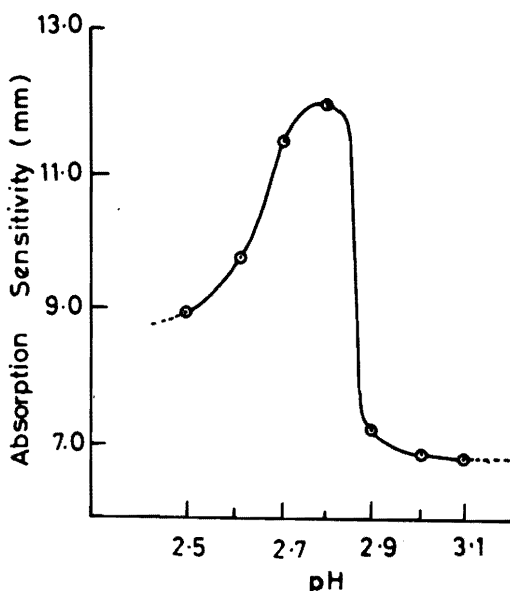


Figure 1. A Typical pH-Dependent Absorption Sensitivity Relationship for Cadmium–Acetophenone System.

Table 1. Absorption Sensitivities And Enhancement Factors Measured At Optimized Fuel, Air and pH Conditions For Various Systems

Metal/Solvent	Fuel Flow (l/min)	Air Flow (l/min)	pH	Absorption Sensitivity (mm)		Enhancement Factor
				(a)	(b)	
Cd/Acetophenone	0.7	6.7	2.8	10.0	3.5	2.9
Pb/Acetophenone	0.7	5.6	2.8	4.0	1.0	4.0
Cd/Amyl acetate	0.7	8.0	2.9	10.0	2.0	5.0
Pb/Amyl acetate	0.7	8.0	2.9	3.0	1.0	3.0
Cd/Butyl acetate	2.0	5.6	2.9	21.0	2.0	10.5
Pb/Butyl acetate	0.5	6.7	2.9	6.5	0.5	13.0
Cd/Diethyl malonate	0.7	5.6	2.5	3.0	0.5	6.0
Pb/Diethyl malonate	0.7	5.6	2.5	7.0	1.0	7.0
Cd/MIBK	0.7	5.6	2.8	69.0	3.5	19.7
Pb/MIBK	0.7	5.6	2.8	10.0	2.5	4.0
Cd/Propyl acetate	2.0	5.6	2.8	5.0	2.5	2.2
Pb/Propyl acetate	2.7	3.3	3.1	16.5	3.5	4.7

(a) Chelation/extraction method; (b) Aqueous-phase, direct method.

Any slight variation in pH changes the absorption sensitivity drastically. In fact, this is a general behavior exhibited by all the solvent systems.

Examination of the listed absorption values reveals that the maximum absorption sensitivity (measured proportional to absorption peak height in mm in contrast to direct absorption scale values having a minimum readability of unit absorption) is obtained in the case of Cd–MIBK system. Next to MIBK for the extraction of cadmium is butyl acetate, which gives an absorption sensitivity of 21.0 mm. Acetophenone and amyl acetate come next in the series with absorption sensitivity at 10.0 mm each. Diethyl malonate is found to be the least desirable solvent for the cadmium extraction. The case of lead, however, is uniquely different compared to that of cadmium. No single solvent gives lead extraction to the extent given by Cd–MIBK system. The maximum absorption obtained for lead is given by propyl acetate for which the absorption sensitivity is 16.5 mm, which is about 25% of the optimum cadmium extraction.

Since the increase in absorption sensitivity for a given metal has been measured in comparison to the corresponding absorption for an aqueous system of the same concentration, the enhancement factors listed in Table 1 stand for the ratio of the absorption value for a metal–solvent system to the

absorption value for the aqueous system at the same concentration, both measured at optimum conditions. Based on the calculated enhancement factors, it can be inferred that the best solvent for the extraction of cadmium is MIBK. However, the extraction ability of MIBK for lead is not promising under the conditions of the present study; its enhancement factor being 13.0 as compared with relatively smaller factors for other solvents. On the whole, butyl acetate has been found to be a better extracting solvent for both lead and cadmium; the enhancement factors being 10.5 and 13.0, respectively. Percent recovery data and comparison of estimated concentrations of cadmium and lead in various locally available drinking waters are given in Table 2. The listed values are cited for repeated measurements on a given sample. The observed recovery in each case is found to be greater than 80%. Relative analytical measurements normally need not take into account percentage recoveries since a one-step extraction under defined conditions of separation relative to the other under the same conditions would always yield the same quantitative results. This is true for atomic absorption work where both standards and unknown solutions are subjected to a relative measurement. Nonetheless, an attempt was made during the present work to quantify the extent of extraction for a water sample

Table 2. Percent Recoveries and Comparison of Estimated Cd and Pb Concentrations in Various Drinking Waters

Water Sample	Nature of Sample	Estimated Concentration $\mu\text{g/l}$		Percent Recovery $\mu\text{g/l}$	
		Cd*	Pb**	Cd	Pb
S-1	Upper-tank, municipal supply; untreated	1.57	2.16	83.9	81.2
S-2	Tube-well supply, untreated	8.25	4.37	84.5	82.4
S-3	Open surface, dam water; treated	7.00	5.85	83.8	81.7
S-4	Shallow well water (40' deep); untreated	7.62	4.06	85.0	82.7
S-5	Natural spring water; open reservoir; untreated	12.53	15.33	84.1	80.1
S-6	City tap-water; treated	5.05	7.80	83.7	81.3
S-7	Natural stream water; untreated	6.90	8.60	84.8	82.8

*Based on MIBK extraction; **Based on butyl acetate extraction

having a predetermined lead and cadmium concentration. It was observed through the comparison of direct aqueous and extracted organic phase aspirations under optimum conditions of pH and fuel-air flow rates, that about 80% recovery of lead is possible in a single extraction step for the MIBK system, while the recovery of cadmium is found to be about 85%.

In conclusion, the proposed acid-medium, ADPC-based chelation-solvent extraction method based on the use of glacial acetic can be applied for the single-step estimation of lead and cadmium in drinking waters under sets of optimum conditions established to this effect. The use of acetic acid in place of hydrochloric acid [13] has the advantage that lead and cadmium acetates are by far more soluble in the aqueous phase than corresponding chlorides. The proposed method has the additional advantage that it does not require any buffer solutions and can be advantageously applied to the estimation of other trace metals.

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