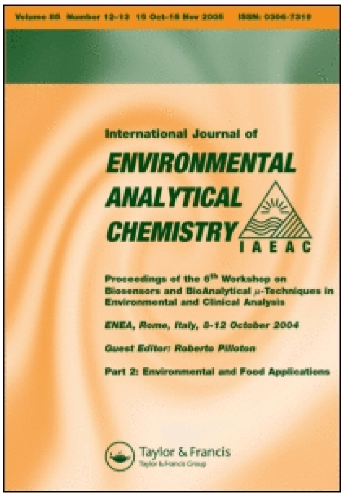

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Determination of Some Transition Metals by Atomic Absorption Spectroscopy after Extraction with Pyridine-2-aldehyde-2-quinolylhydrazone†

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The extraction of pyridine-2-aldehyde-2-quinolylhydrazone chelates of cadmium, cobalt, copper, nickel, and zinc into isoamyl alcohol (IAOL) and methylisobutyl ketone (MIBK) has been investigated as a basis for the determination of these metals. Below pH 6 the extraction is enhanced by the addition of perchlorate, suggesting that charged complexes are being extracted by ion-pair formation. Sensitivities (1% absorption) are reported for IAOL and MIBK solutions of the metals sprayed into an air–acetylene flame. A procedure for the determination of the above metals by atomic absorption spectroscopy after extraction is given. The procedure is applied to the analysis of tap water for cadmium, copper, and zinc.

INTRODUCTION

Substituted heterocyclic hydrazones form chelates with a number of transition metals which are extractable into immiscible organic solvents. Because of the high molar absorptivities of the resulting chelates, spectrophotometric techniques have been applied until now. Pyridine-2-aldehyde-2-quinolylhydrazone (PAQH) has been used for the photometric determination of palladium,[1,2] cobalt, and nickel.[3,4] Quinoline-2-aldehyde-2-quinolylhydra-

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zone (QAQH) has found use for the determination of copper,[5,6] and zinc has been determined with phenanthridine-6-aldehyde-2-quinolylhydrazone.[7] Under controlled conditions the procedures developed were specific for the metals involved; the use of masking agents and/or careful pH control was necessary because of the similarity of the chelate spectra.

In this work attention is focused on the atomic absorption determination of cadmium, cobalt, copper, nickel, and zinc after extraction with PAQH. An investigation of the extractability of the PAQH chelates of the above metals has been made by three of the authors.[8]

EXPERIMENTAL

Reagents and apparatuses

Solutions of cobalt, copper, nickel, and zinc were prepared from Fisher Certified Atomic Absorption Standards; cadmium solutions were prepared by dissolving the reagent-grade metal in dilute nitric acid. Reagent-grade or redistilled solvents were used. PAQH was prepared as previously described;[9] a 1% solution in 0.05 *M* hydrochloric acid was stable indefinitely. Solutions of the reagent in organic solvents were freshly prepared daily. All other chemicals were of reagent-grade quality.

Spectra were measured with Bausch & Lomb Spectronic 505 and Unicam 8000 Spectrophotometers. A Beckman 1301 DB-G Atomic Absorption Spectrophotometer was used for atomic absorption measurements. Perkin–Elmer single-element hollow cathode lamps were used for cobalt, copper, cadmium, and nickel; a calcium–zinc multielement lamp was used for zinc. Measurements of pH were made with a Radiometer 28 pH meter.

Procedure

a) Spectrophotometric work Aqueous solutions of the metals containing PAQH, acetate buffer, and sodium perchlorate were shaken with an approximately equal volume of organic solvent alone or containing PAQH. Equilibrations were done in separatory funnels or test tubes with ground glass stoppers, using a mechanical shaker or home-made rotator. Manual shaking was used for short equilibration times. Equilibrium was established within two minutes for those systems in which the reagent was added as an aqueous solution in dilute hydrochloric acid, while longer shaking times (3–4 hours) were required when the reagent was added as a solution in the organic solvent. An aliquot of the extract was taken for spectrophotometric measurements.

b) Interference study and tap water analysis Aqueous solutions of the metals (100 ml) containing 0.08 mmole of PAQH (added as a 1% solution in

0.05 M HCl), 0.5 mmole of sodium perchlorate, and acetate buffer were shaken with 10 ml of isoamyl alcohol (IAOL) or methylisobutyl ketone (MIBK) for two minutes. A pH of 5–6 was used for the extraction of copper, cobalt, and nickel; zinc and cadmium were extracted at pH 6–8. After allowing the phases to separate for 30 minutes, the extracted metals were determined by atomic absorption. The MIBK extracts were directly aspirated; the IAOL extracts were diluted with an equal volume of ethanol before aspirating. Calibration curves were prepared by extracting known quantities of the metals under the same conditions.

RESULTS AND DISCUSSION

The optimum pH ranges for the extraction of the metals under the conditions used for the water analyses are shown in Figures 1 and 2. It was found that if perchlorate is not present, the recovery of all metals is considerably less at pH < 6 (MIBK solvent). This suggests that in the lower pH region the metals are extracted partially or wholly as ion-pair complexes with perchlorate, and

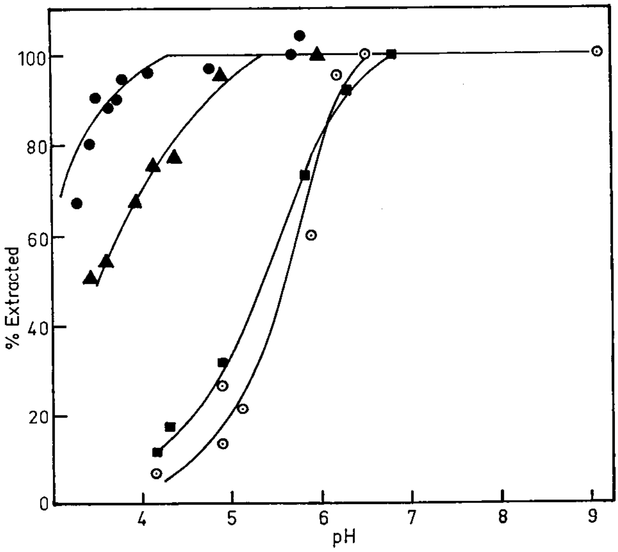

FIGURE 1 PAQH extraction of copper, cadmium, and cobalt into MIBK 0.08 mmole PAQH, V_w = 100 ml, V_0 = 8 ml.

● 15 mcg copper, 0.5 mole sodium perchlorate added

○ 15 mcg copper, no perchlorate added

■ 6 mcg cadmium, 0.5 mmole sodium perchlorate added

▲ 45 mcg cobalt, 0.5 mmole sodium perchlorate added

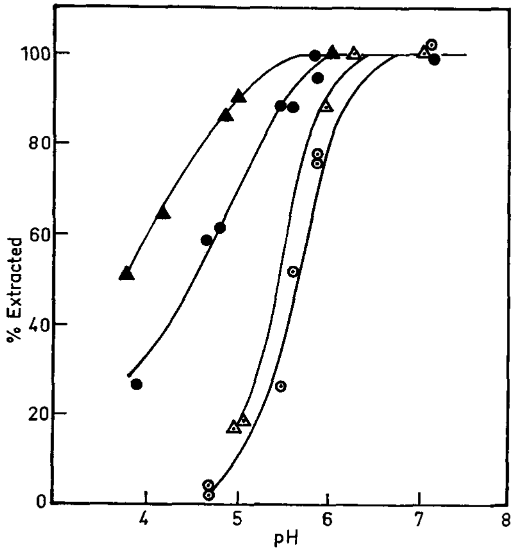

FIGURE 2 PAQH extraction of nickel and zinc into MIBK 0.08 mmole PAQH, $V_w = 100$ ml, $V_0 = 8$ ml.

▲ 40 mcg nickel, 0.5 mmole sodium perchlorate added
△ 40 mcg nickel, no perchlorate added
● 5 mcg zinc, 0.5 mmole sodium perchlorate added
○ 5 mcg zinc, no perchlorate added

the chelates must therefore be charged species. Such behavior has been observed previously for cobalt,[8] and the extracted cobalt species has been proposed to be $(Co^{III}Q^+)(ClO^-)$, where Q = deprotonated PAQH (HQ and H_2Q^+ will be used to indicate the neutral and doubly protonated reagent, respectively). An explanation for the metals having +2 oxidation states may be the formation of protonated complexes in which PAQH is acting as a neutral ligand, e.g. $M^{II}(HQ)_2^{2+}$ or $M^{II}(HQ)(Q)^+$. As the pH is raised these complexes presumably become deprotonated, forming neutral species which are extractable in the absence of perchlorate. Geldard and Lions[10] have demonstrated the formation of protonated and deprotonated complexes for the ligand pyridine-2-aldehyde-2-pyridylhydrazone (PAPHY) and analogous reagents. Heit and Ryan[1] reported the extraction of palladium into chloroform as $Pd(HQ)SO_4$; however, in an earlier paper[9] on PAQH chelates they reported no evidence for protonated complexes.

The visible spectra of the extracted metal complexes are similar, having maxima between 480 and 520 nm. The reagent absorbs only slightly in this region. Spectro-photometric sensitivities are considerably less for cadmium and zinc than for the other metals under the conditions used in the water analyses, thus atomic absorption offers a real advantage for the determination of these two metals after PAQH extraction. The effective molar absorptivities of the chelates in MIBK depends upon the pH of the solution from which they were extracted, and for this reason they are not reported here. Figure 3 shows an example of this behaviour for the nickel–PAQH system. Under the experimental conditions the nickel was 95–100% extracted (even at pH 4.6) because of the larger solvent:water ratio than was used in the analytical procedure. This pH dependence further suggests the formation of different species in the low and high pH ranges.

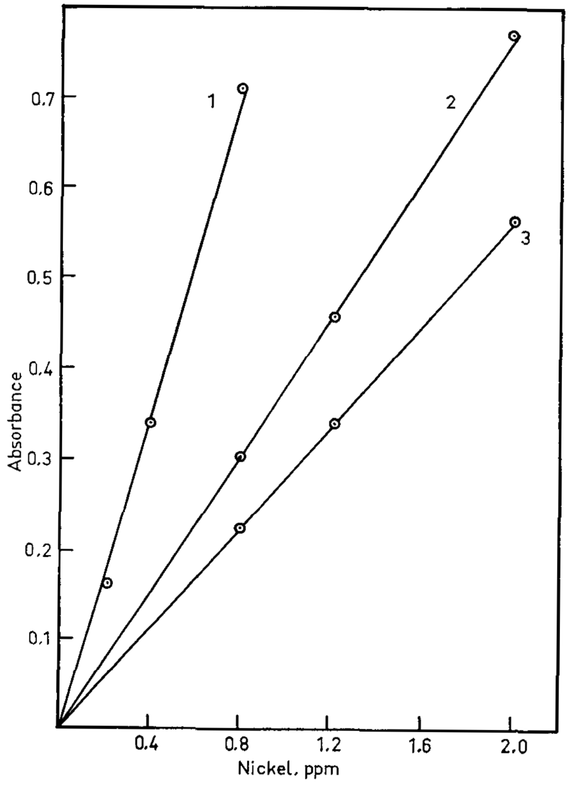

FIGURE 3 Absorbance of nickel–PAQH complexes extracted at different pH values. $V_w = 8$ ml, $V_0 = 5$ ml, 0.0064 mmole PAQH

1. no perchlorate, pH 6.7
2. 0.04 mmole sodium perchlorate added, pH 5.0
3. 0.04 mmole sodium perchlorate added, pH 4.6

Of the solvents used in this work, MIBK is the most suitable for atomic absorption work. The more viscous solvent IAOL should be diluted with ethanol before aspiration and has the added disadvantage of having a higher solubility in water than MIBK. Although the chelates are extractable into benzene, this solvent is unsuitable for atomic absorption work because it produces a smoky yellow flame. Atomic absorption sensitivities (1 % absorption) are given in Table I.

TABLE I

Sensitivities (1 % absorption) for atomic absorption determination

Metal	Wavelength nm	Lamp current ma	Slit mm	IAOL ppm[a]	MIBK ppm
Cd	228.8	5	0.25	0.016	0.012
Co	240.7	15	0.10	0.060	0.045
Cu	324.8	10	0.10	0.025	0.040
Ni	232.0	20	0.25	0.040	0.083
Zn	231.9	10—15	0.50	0.007	0.007

Working conditions: laminar flow, 10-cm lean air-acetylene flame, cold mode, single pass

[a] In the presence of 50% v/v ethanol.

The effect of several cations commonly found in natural waters is shown in Table II. The presence of large quantities of metals which react with PAQH may be troublesome due to excessive consumption of the reagent. However, the presence of 100-mcg quantities of cadmium, cobalt, copper, nickel, lead, zinc, manganese(II), and iron(III) as interfering metals is easily tolerated. Strong complexing agents such as cyanide and EDTA will probably interfere.

TABLE II

Atomic absorption determination of Cd, Co, Cu, Ni, and Zn

Foreign elements	Metal	Taken, mcg	Found, mcg
100 mcg Fe(III), Co, Ni	Cd	4.0	4.2
200 mcg Fe(III), Co, Ni		6.0	6.6
100 mcg Cu, Zn, Pb, Mn(II)		2.0, 2.0	2.2, 2.0
200 mcg Cu, Zn, Pb, Mn(II)		4.0	4.5
100 mcg Fe(III), Co, Ni, 1.3 mg Cr(III), 1.7 mg Al(III)		2.0	1.8
100 mcg Fe(III), Co, Ni, Cu, Zn, Pb, Mb(II)		4.0	4.0
1.1 mg Mg, 1.3 mg Cr(III), 1.3 mg Ca, 1.7 mg Al(III)		6.0	6.1

TABLE II—*cont.*

Foreign elements	Metal	Taken, mcg	Found, mcg
none	Co	3.0	3.4
		6.0	5.4
100 mcg Fe(III), Cu, Ni, Pb, Mn(II)		0.0	0.0
		4.0	4.1
100 mcg Fe(III), Cu, Cd, Ni, Pb, Zn, Mn(II)		0.0	0.0
		2.0	2.0
		4.0	4.4
200 mcg Fe(III), Cu, Cd, Ni, Pb, Zn, Mn(II)		2.0	2.0
		4.0	4.2
		6.0	6.7
100 mcg Fe(III), Cu, Cd, Ni, Pb, Zn, Mn(II), 0.9 mg Al(III), 1.3 mg Cr(III), 1.5 mg Ca, 1.1 mg Mg		2.0	1.8
		4.0	4.2
		10.0	11.0
100 mcg Fe(III), Co, Cd, Ni, Pb, Zn, Mn(II)	Cu	4.0	4.2
200 mcg Fe(III), Co, Cd, Ni, Pb, Zn, Mn(II)		12.0	11.6
1.1 mg Mg, 1.3 mg Ca		8.0	8.3
1.3 mg Cr(III), 1.7 mg Al(III)		8.0	8.3
1.1 mg Mg, 1.3 mg Cr(III), 1.7 mg Al(III)		4.0	4.0
100 mcg Fe(III), Co, Ni, Cd		8.0	8.0
200 mcg Pb, Zn, Mn(II)		12.0	11.7
100 mcg Cd, Ni, Pb, Zn, Mn(II)		4.0	4.2
100 mcg Fe(III), Co, Ni, Pb, Zn, Mn(II), 1.1 mg Mg, 1.3 mg Cr(III), 1.3 mg Ca, 1.7 mg Al(III)		0.0	0.0
		12.0	12.2
1.1 mg Mg, 1.3 mg Ca	Ni	10.0	10.5
1.3 mg Cr(III), 1.7 mg Al(III)		20.0	18.5
200 mcg Fe(III), Co, Cd, Cu, Pb, Zn, Mn(II)		10.0	10.0
300 mcg Cd, Pb, Zn, Mn(II)		20.0	19.5
500 mcg Fe(III), Co		10.0	10.0
200 mcg Fe(III), Co, Cd, Cu, Pb, Zn, Mn(II), 1.1 mg Mg, 1.3 mg Ca, 1.3 mg Cr(III), 1.7 mg Al(III)		0.0	0.0
		15.0	13.5
1.7 mg Al(III)	Zn	2.0, 2.0	1.9, 1.9
1.1 mg Mg, 1.3 mg Ca, 1.3 mg Cr(III), 1.7 mg Al(III)		1.0	1.0
100 mcg Cd		2.0	2.0
200 mcg Pb		3.0	3.0
200 mcg Mn(II)		3.0	3.0
200 mcg Fe(III), Co, Ni		3.0	2.7

Application of the method

Filtered laboratory tap water was analyzed for cadmium, copper, and zinc by the above procedure, using MIBK as the extracting solvent. Results are given in Table III. The cadmium content of the tap water was below the detection limits of this procedure.

TABLE III

Analysis of tap water[a] by atomic absorption after PAQH extraction of metals into MIBK

	Metal added, mcg	Metal found, mcg	Recovery of added metal, mcg	% Recovery
	0.0	0.0		
	0.0	0.0		
	0.0	0.0		
	2.0	1.7	1.7	85
Cd	2.0	1.8	1.8	90
	4.0	3.7	3.7	93
	4.0	3.5	3.5	88
	4.0	4.0	4.0	100
				91 mean
	0.0	3.4		
	0.0	3.2		
	0.0	3.5		
Cu	2.0	5.7	2.3	115
	4.0	7.6	4.2	105
	4.0	7.6	4.2	105
				108 mean
	0.0	0.5		
	0.0	0.5		
Zn	1.0	1.5	1.0	100
	2.0	2.4	1.9	95
	3.0	3.4	2.9	97
				97 mean

[a] 100-ml. volumes.

CONCLUSIONS

Pyridine-2-aldehyde-2-quinolylhydrazone has been shown to be a useful semiselective scavenging reagent for use in atomic absorption spectroscopy. Because it complexes a relatively small number of metals, it may find use in situations where large quantities of a particular metal would lead to excessive consumption of a less selective reagent such as ammonium pyrrolidinedithiocarbamate (APDC) or dithizone. PAQH is also more stable in solution than these two reagents.

The procedure described in this paper was developed for a 100-ml sample and gives a concentration factor of 12.5 (since the solubility of MIBK in water is about 2%). Slight modifications should allow the procedure to be applied to larger sample volumes.

Acknowledgements

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