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Short Communication

LIQUID-LIQUID EXTRACTION WITH 2-ACETYLPYRIDINEBENZOYLHYDRAZONE IN THE DETERMINATION OF TRACES OF COPPER, NICKEL, COBALT AND ZINC BY ATOMIC ABSORPTION SPECTROMETRY

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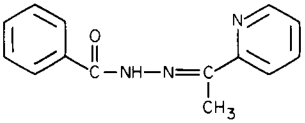
Summary. Trace amounts of Cu, Ni, Co and Zn in aqueous solutions are determined by their simultaneous extraction with 2-acetylpyridinebenzoylhydrazone followed by flame atomic absorption spectrometry. Isoamyl alcohol is the preferred solvent. Calibration graphs are linear, usually over the range 0—0.2 mg l^{-1} of aqueous phase. There are few interferences from other ions present in 500—1000-fold amounts.

Many atomic absorption spectrometric (a.a.s.) procedures, based on the separation and preconcentration of metal ions by liquid-liquid extraction have been reported [1]. Among the commonly used chelating reagents are sodium diethyldithiocarbamate [2], ammonium pyrrolidinedithiocarbamate [3], 8-quinolinol [4] and dithizone [5]. 4-Methylpentan-2-one is usually preferred as the solvent for a.a.s. but other solvents such as chloroform, ethyl acetate, butyl acetate and isoamyl alcohol have also been used [1].

Aroylhydrazones behave as polydentate ligands forming uncharged chelates with divalent transition metal ions [6], which can be extracted into organic solvents. These compounds have been widely employed in spectrophotometric and fluorimetric methods for the determination of metals [7] but have rarely been applied in a.a.s. methods [8].

This communication describes a sensitive method for the determination of trace amounts of copper, nickel, cobalt and zinc by flame a.a.s. after extraction with 2-acetylpyridinebenzoylhydrazone (I; APBH) and isoamyl alcohol. The metal—APBH complexes are reasonably stable in isoamyl alcohol. Optimal conditions for the extraction are described.



(I)

Experimental

Instrumentation. The Pye-Unicam SP-9 atomic absorption spectrometer used was equipped with a standard air-acetylene burner head. Single-element (copper, zinc, cobalt and nickel) hollow-cathode lamps were used with deuterium background correction. The instrumental settings are summarized in Table 1. Other instrumentation included a Perkin-Elmer 575 spectrophotometer with 1.0-cm quartz or glass cells, and a Metrohm E-516 pH meter with a combined glass—calomel electrode.

Reagents. Stock standard solutions (1.000 mg ml^{-1}) were prepared by dissolving 1.000 g of pure metal in the minimum volume of an appropriate mineral acid. Single- and multi-element solutions of lower concentrations were prepared by appropriate dilution as required.

Solutions (0.05% and 0.1% w/v) of APBH in ethanol, isoamyl alcohol, 4-methylpentan-2-one ketone (MIBK) and n-butyl acetate were prepared. The solutions in MIBK are stable for a day, those in isoamyl alcohol for a month and those in the other solvents for a few days. The synthesis of PABH has been described elsewhere [9].

Potassium hydrogenphthalate/sodium hydroxide (0.1 M, pH 6.0) and other buffer solutions were prepared conventionally. All reagents were of analytical grade and all solutions were prepared with distilled deionized water.

Glassware was cleaned with dithizone dissolved into chloroform and all reagent solutions were stored in polyethylene bottles, previously soaked for several days in 6% (v/v) nitric acid. Special care was taken to avoid potential sources of contamination from the materials and chemicals used.

Procedure. An aliquot of the sample solution (containing up to 100 μg of each metal ion) was mixed with 5 ml of phthalate buffer solution (pH 6.0), diluted to 100 ml with water in a 250-ml separatory funnel and extracted with 10 ml of a 0.05% (w/v) solution of APBH in isoamyl alcohol for 2 min. After 5 min or more, to allow phase separation, the aqueous layer was discarded and the organic phase was dried with anhydrous sodium sulfate and transferred into stoppered glass tubes for a.a.s. (see Table 1).

TABLE 1

Conditions for atomic absorption spectrometry[a]

	Cu	Ni	Co	Zn
Analytical line (nm)	324.8	232.0	240.7	213.8
Spectral bandwidth (nm)	0.5	0.2	0.2	0.5
Lamp current (mA)	4	12	12	8
Integration time (s)	2	2	2	3
Zero set	IA	IA	IA	BR[b]

[a]Air and acetylene flows were 5.2 and 1.2 l min^{-1}, respectively. Background correction was used only for zinc. [b]Blank reagent.

Calibration graphs were prepared by using multielement standard solutions of appropriate volumes, covering the ranges 0.1—1 (Co), 0.1—2 (Ni and Zn) and 0.1—3 (Cu) μg ml^{-1} in the organic phase, treated in exactly the same way as the samples.

Results and discussion

Spectrophotometric study of the metal—APBH chelates. When diluted solutions of metal ions in acidic or alkaline medium and a 0.1% (w/v) of APBH in ethanol are mixed, a yellow chelate is formed immediately. Spectrophotometric characteristics of the cobalt, nickel, copper and zinc complexes are detailed in Table 2. At the optimum pH values, many other metal—APBH complexes are also formed in aqueous ethanol. However, because a high proportion of ethanol is required to dissolve the metal—APBH complexes, liquid-liquid extraction is advisable. The extraction was used satisfactorily with flame a.a.s., providing increased sensitivity and selectivity.

Extraction/a.a.s. study. The effect of pH on the extraction of the metal chelates into different solvents was studied over the pH range 2—11 (Table 3). Isoamyl alcohol proved to be the most satisfactory, because the APBH reagent solution was more stable and the a.a.s. signals were more reproducible. To control the pH, 2.5 ml of the phthalate buffer was added when the phase/volume ratio was less than 5, and 5 ml when it exceeded 5.

TABLE 2

Spectrophotometric characteristics of the metal—APBH chelates in aqueous ethanol

Metal ion	λ_{max} (nm)	ϵ (l mol^{-1} cm^{-1})	Optimum pH	Metal—APBH ratio
Cu(II)	365—375	3.1×10^4	2.5—3.5 (6.8—7.5)	n.d.[a]
Zn(II)	375	3.4×10^3	6.8—9.0	1:3
Ni(II)	376	2.5×10^4	5.3—8.3	1:3
Co(II)	362—370	1.5×10^4	6.3—7.0 (8.5—9.0)	1:3

[a] Not determined.

TABLE 3

Optimum pH ranges for the solvent extraction of the metal—APBH chelates

Metal ion	n-Butyl acetate[a]	Isoamyl alcohol	MIBK
Cu(II)	—	5—8	5.5—8
Zn(II)	5—8	4—7.5	5—11
Ni(II)	—	5—8	4.7—7.5
Co(II)	—	5—9	6—10

[a] Atomic signals of Cu, Ni and Co were not reproducible.

In other tests, the shaking time was varied from 0.5 to 5 min; 2 min was sufficient to provide the maximum a.a.s. signals. A period of 5 min was usually enough for phase separation. An aliquot of 100 ml of solution containing 5 μg of each metal ion was extracted with 10 ml of 0.01—0.1% (w/v) APBH solution in isoamyl alcohol. Changes in the reagent concentration over this range did not affect the a.a.s. signals; 10 ml of 0.05% (w/v) reagent solution was chosen, in order to overcome interferences.

A 10:1 V_w/V_o ratio was selected to provide reasonable sensitivity and precision. If this ratio were higher, insufficient organic phase would be obtained after extraction because of the solubility of isoamyl alcohol in water.

The extraction efficiency was calculated from four 100-ml aliquots, all of which contained 10 μg of each metal. These solutions were extracted with 10 ml of APBH in isoamyl alcohol; the dried organic layers were then carefully evaporated to dryness, and the residues were dissolved in 5 ml of hot 4 M nitric acid. The recoveries of copper, nickel and cobalt, calculated from their a.a.s. signals in these solutions, were higher than 92% in all cases. The zinc recovery was calculated from a spectrophotometric method with dithizone [10] and was found to exceed 90%.

The atomic absorption signals of the metal complexes remained constant for at least two days when the samples were stored between measurements at 4°C.

Atomic absorption determination of copper, nickel, cobalt and zinc. Under the recommended conditions, linear calibration graphs were obtained for the ranges 0—10 μg (Co), 0—20 μg (Ni and Zn) and 0—30 μg (Cu). The sensitivities for 1% absorption were 0.055, 0.063, 0.040 and 0.049 μg ml^{-1} related to the organic layer, for Co, Ni, Cu and Zn, respectively.

The precision of the method was checked for 5 aliquots containing 10 μg and 6 aliquots containing 5 μg of each metal ion. The relative standard deviations for 10-μg contents were ±0.74% (Co), ±0.62% (Ni), ±0.60% (Cu) and ±1.00% (Zn), and for 5-μg contents ±1.44% (Co), ±2.82% (Ni), ±1.0% (Cu) and 3.90% (Zn).

Influence of other ions. Copper, nickel, cobalt and zinc (5 μg of each metal ion per 100 ml of aqueous solution) were determined in the presence of 1000-fold amounts of 42 ionic species. There were no interferences from Na, K, Ca, Mg, Pb, Cd, Mn(II), Mo(VI), W(VI), V(V), As(V), NO_3^-, NO_2^-, Cl^-, F^-, Br^-, I^-, SCN^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, oxalate, tartrate and citrate. Thallium(I), Be, Al, Cr(III), La and borate did not interfere in the determinations of nickel, cobalt and copper. In the determination of zinc, 1000-fold amounts of La(III) (in the presence of tartrate) and Al(III) and Tl(I) (both in the presence of fluoride) were tolerated; Cr(III) and Be(II) in the presence of fluoride were tolerated in 500- and 100-fold amounts, respectively. Thorium(IV) and Zr(IV) in 1000-fold amounts interfered in the determinations of cobalt and zinc but could be masked with tartrate; they did not interfere in the determinations of nickel and copper.

When iron(II, III), U(VI), Sb(III) and Ti(IV), which react with the reagent, were present in 1000-fold amounts, a higher concentration of reagent (0.1—0.2% w/v) was required in order to achieve the total extraction of copper, nickel, cobalt and zinc. Under analogous conditions bismuth may be present in 250-fold quantities.

The main advantage of the proposed method is its sensitivity and simplicity. In contrast to most other methods, one extraction is sufficient for the determination of Cu, Ni, Co and Zn in a sample. Furthermore, samples can be extracted immediately after they have been taken and the extracts stored for a couple of days, thereby alleviating transport problems.

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