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Fresenius J Anal Chem (1994) 350:650–651 – © Springer-Verlag 1994

Coprecipitation study of As(III), Cu(II) and Cd(II) from aqueous solution using 5-bromo and 2-methylthioquinoline-8-thiol

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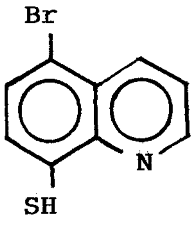
Received: 5 November 1993/Accepted: 20 June 1994

Abstract. Oxidation products of 5-bromo and 2-methylthioquinoline-8-thiol are used for the quantitative coprecipitation of As(III), Cu(II) and Cd(II) from water solutions in a wide range of acidity. The recovery is >95%.

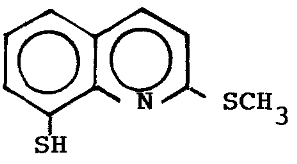
Introduction

Organic disulphides, obtained by oxidation of –SH containing organic reagents, have been used for the selective liquid liquid extraction of Cu(I), Se(IV), Te(IV), Pd(II) and several other elements for their subsequent spectrophotometric determination. A new application of these compounds is their use as coprecipitators for multi-element preconcentration in the analysis of natural water and inorganic salts and for the purification of the latter [1, 2]. The coprecipitation is based on the formation of water insoluble inner complex compounds of the trace elements with the –SH group containing reagent and the formation of disulphide directly in the solution owing to the easy oxidizability of the –SH group. During the formation of the solid disulphide phase the trace elements are coprecipitated.

Previous studies [1] have shown that it is not possible to coprecipitate As(III) with quinoline-8-thiol (QT). Therefore two other reagents have been chosen which have a stronger acid behaviour than QT, in order to concentrate As(III) as well as Cu(II) and Cd(II). This paper contains the results of coprecipitation studies with 5-bromoquinoline-8-thiol (BQT: reagent I) and 2-methylthioquinoline-8-thiol (MTQT: reagent II) for the concentration of the above elements from water solutions.



BQT: reagent I



MTQT: reagent II

Experimental

The study was performed using radiotracers (^{64}Cu, ^{72}As, ^{115}Cd).

The coprecipitation was carried out as described previously [1, 2]. The free reagent I in ethanol and the sodium salt of the reagent II in 3 mol·L^{-1} NaOH were prepared daily. The synthesis of these reagents has been described [3, 4].

A 1%m/V aqueous solution of hydrogen peroxide was also prepared daily. Coprecipitation was carried out from 100 mL of

Table 1. pH-Ranges and maximum recovery yields of the coprecipitation of inner complex compounds of As(III), Cu(II) and Cd(II)

Elements	5-Bromoquinoline-8-thiol			2-Methylthioquinoline-8-thiol		
	pH-range	Yield (%)	SD	pH-range	Yield (%)	SD
As(III)	0.2–10.2	96	3	2 mol·L^{-1} HCl, pH 8.0	95	3
Cu(II)	0.2–10.1	97	4	0.2–10.3	97	2
Cd(II)	1.3–10.0	96	3	1.5–9.6	96	4

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water solution using 15 mg of reagents I or II and 1 mL of H_2O_2 solution.

Results and discussion

The maximum formation of solid phase from the oxidation products of BQT and MTQT occurs in the range from $1\ \mathrm{mol \cdot L^{-1}}$ HCl to pH 11 or from $2\ \mathrm{mol \cdot L^{-1}}$ HCl to pH 11, respectively. In water solution AsO_3^{3-} forms unstable compounds with QT which are not extracted into chloroform and are not coprecipitated with bis(8-quinolyl)disulphide (the oxidation product of QT). AsO_4^{3-} in acid media oxidizes QT and its derivatives to the corresponding disulphides. As(III) forms stable inner complex compounds with the derivatives of QT such as BQT and MTQT. The data show that the coprecipitation of As(III), Cu(II), and Cd(II) occurs with bis(5-bromo-8-quinolyl) and bis(2-methylthio-8-quinolyl)disulphides over a wide range of pH (see Table 1). Selective coprecipitation of As(III) using MTQT is also possible. In water solution MTQT has a solubility of $3 \times 10^{-5}\ \mathrm{mol \cdot L^{-1}}$, which is significantly less than the solubility of BQT ($1.5 \times 10^{-4}\ \mathrm{mol \cdot L^{-1}}$) [5]. Therefore the reagent precipitates in aqueous solution of pH 5–6. In this case a combined collector for the coprecipitation of the complexes of the trace elements is used. The coprecipitator contains the insoluble part of MTQT and its oxidation product. It has been found that the insoluble part of the reagent provides a recovery yield of 67–73% for the coprecipitation of the elements mentioned. The latter data are obtained if the coprecipitation is carried out without using H_2O_2. This concentration technique is characterized by high coprecipitation efficiency. For instance, the minimum amount of BQT for complete coprecipitation of As(III) from 3 L of seawater is 97 mg. Preconcentration factors of $> 10^4$ are obtained.

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Fresenius J Anal Chem (1994) 350:651–652 – © Springer-Verlag 1994

Determination of molybdenum in silicates by flame atomic absorption spectrometry exploiting activated carbon as collector

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Received: 27 September 1993/Accepted: 25 May 1994

Abstract. An analytical procedure has been developed for molybdenum determination in geological silicate materials using flame atomic absorption spectrometry (injection method), after sorption of the molybdenum-ammonium pyrrolidinedithiocarbamate complex (MoAPDC) on activated carbon.

Introduction

Since its introduction in analytical chemistry, activated carbon has been used as a collector allowing separation and determination of low levels of analytes in such matrices as high-purity substances, water and rocks. Sorption on activated carbon of dissolved chemical species was studied for several elements. In most cases, suitable pH adjustment of the solution is all that is required [1–7]. However it was shown that, in the presence of a chelating or precipitating agent, metal retention can be improved [8]. The mechanism of this sorption is still under investigation. According to Sigworth and Smith [9] three mechanisms are probably involved: physical adsorption due to the high surface area of activated carbons; ion-exchange due to the small number of oxygen complexes and other functional groups fixed on the carbon surface and precipitation from a supersaturated solution induced by nucleation by the carbon; this reduces the solubility of a metallic salt. Colloidal suspensions can be also broken by disturbing the surface charge which protects the colloidal particles. In addition, powdered or granular carbon exerts an excellent filtering action.

Experimental

The reference rock samples (granite JB-1 from Geological Survey of Japan (GSJ) and granite GH provided by Centre de Recherches Pétrographiques et Géochimiques, France) were used as received (powdered 200–400 mesh). Granitic rock samples from Piranhas-Goiás, Brazil, were broken and ground in a ball mill grinder until fine powder (150–200 mesh) was obtained. The procedure for the chemical decomposition involved an acid treatment [10, 11]: 1–2 g of powdered sample was treated in a PTFE beaker with 15 ml of 48% hydrofluoric acid and the mixture was allowed to stand for about 1 h.

The beaker was heated on a sand bath (150 °C) until dryness. After cooling, 15 ml of a mixture of concentrated nitric and perchloric acids (3 + 1 v/v) were added and the solution again heated to dryness. The residue was then treated with 2.5 ml of concentrated hydrochloric acid, water and 4 drops of 30% hydrogen peroxide with gentle warming to achieve complete solubilization. After making up to 50 ml, the pH of the so-

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