

Flame AAS determination of trace amounts of Cu, Ni, Co, Cd and Pd in waters after preconcentration with 2-nitroso-1-naphthol

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Flame AAS was applied to the determination of micro trace amounts of Co, Ni, Cu, Cd and Pd in waters after precipitation of their complexes with 2-nitroso-1-naphthol. The precipitate was separated from the sample solution by filtration through Millipore filter of 0.22 μm pore size under suction. It was dissolved with a minimum amount of ethanol and was subjected to flame AAS analysis. The detection limits of Co, Ni, Cu, Cd and Pd were 0.61, 0.64, 0.89, 0.10 and 0.60 $\mu\text{g l}^{-1}$, respectively. The method was validated using the reference material SPS-WW2 – Spectrapure Standards, Norway, and was applied for analysis of capture water and waste water.

Keywords: Flame AAS, preconcentration, 2-nitroso-1-naphthol, waters, Co, Ni, Cu, Cd, Pd

INTRODUCTION

Waters are among the most often analyzed samples. A large number of elements occur as contaminants from natural processes, industrial activities and automobile traffic. The determination of the toxic trace elements Cd, Co, Cu, Ni and Pd in natural and waste waters is of significant interest in the monitoring of environmental pollution. The use of atomic absorption spectrometry for direct trace and ultra-trace analysis of these waters meets specific difficulties – e.g., insufficient sensitivity (flame AAS) or severe matrix interferences (graphite furnace AAS) [1]. Therefore, sample pretreatment is usually necessary to separate/preconcentrate trace analytes prior to their AAS detection [2].

Solvent extraction is one of the most widely applied procedures for trace element preconcentration and separation with subsequent flame AAS analysis. The main reason for this is the higher sensitivity of the analysis of organic solutions in comparison with that of aqueous solutions. The trace metal ions are usually extracted as chelate complexes into the organic phase [3]. In solid phase extraction the chelate complexes of the metal ions are collected onto solid sorbents [4–6]. As chelate complexes are insoluble in aqueous solutions, they may be separated from the aqueous phase as precipitates without the addition of a solid sorbent. Depending on the adopted method of

detection, the precipitates, separated by filtration, may be dissolved in a suitable solvent [7–9] or directly analyzed e.g., by X-ray fluorescence spectrometry [10, 11]. An essential advantage of the precipitation procedure is the possibility to handle large sample volumes achieving high preconcentration factors [12].

2-Nitroso-1-naphthol is a chelating reagent that has been used for on-line preconcentration of cobalt on a chelating microcolumn [13], for the spectrophotometric determination of ruthenium [14], as well as for the solid phase extraction of Th, Ti, Fe, Pb and Cr from waters [15]. There are no data in the literature for the preconcentration of Cu, Ni, Cd and Pd with 2-nitroso-1-naphthol.

The purpose of the present work was to study the possibilities for precipitation preconcentration of trace amounts of Cu, Ni, Co, Cd and Pd using 2-nitroso-1-naphthol with a view to their subsequent flame AAS determination. The method developed was validated using a reference material and was applied to the determination of traces of these elements in capture water and waste water.

EXPERIMENTAL

Instrumentation

A Thermo SOLAAR M5 flame atomic absorption spectrometer with deuterium background corrector was used in this study. All measurements were performed in air-acetylene flame under standard conditions except for the 10

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% reduction in the acetylene flow in the analysis of the ethanolic solutions.

Reagents

Analytical grade reagents and redistilled water were used throughout. The stock solutions of Ni, Co, Cu, Cd and Pd of concentration 1000 mg l^{-1} were prepared from Merck titrisols. Intermediate standard solutions were prepared by stepwise dilution of the stock solutions with ethanol. 2-Nitroso-1-naphthol (95%, Fluka), ethanol (96%, Merck), ammonia (25%, Merck), acetic acid (99–100%, Merck) and ammonium acetate (Merck) were used.

Buffer solutions for the pH range 5.0 – 7.0 were prepared from 0.5 mol l^{-1} ammonium acetate and were brought to the needed pH value with dilute ammonia or acetic acid. Durapore® membrane filters (Millipore), cat. No GVWP02500, $0.22 \mu\text{m}$ pore size were employed. A 1 % solution of 2-nitroso-1-naphthol was prepared in ethanol.

The reference material for measurement of elements in waste water SPS-WW2, Batch no.108, Spectrapure Standards AS (Oslo, Norway) was used.

Preconcentration procedure

150 ml of the water sample were mixed with 10 ml of buffer pH 6.5 and 11 ml of 1 % solution of 2-nitroso-1-naphthol. The mixture was stirred for 40 min on a shaking machine. The precipitate formed was filtered under suction through a membrane filter. The precipitate was transferred into a 5 ml volumetric flask, dissolved in ethanol and filled up to the mark with ethanol.

Blank samples were prepared by treating 150 ml of redistilled water in the described way. The calibration solutions were prepared by adding aliquots of the standard solutions of the analytes to precipitates obtained from blank samples prior to their dissolution in ethanol.

For the analysis of the reference material (RM) 20 ml aliquots (2 ml for the determination of Ni and Cu) were diluted to 150 ml with water and supplied with 10 ml buffer pH 6.5 and 11 ml reagent solution. The subsequent steps of the procedure were as described above.

RESULTS AND DISCUSSION

Calibration

The slopes of calibration curves prepared in ethanol and in a 1 % ethanolic solution of 2-nitroso-1-naphthol were compared. It was found that 2-nitroso-1-naphthol considerably suppressed the absorbance of the analyte elements (differences in

the slopes between 20 and 40%). On the other hand, only part of the reagent added to the aqueous phase passed into the final concentrate. In order to eliminate calibration errors due to varying reagent concentrations, the calibration curves were prepared as described in the experimental part.

Effect of pH of complexation

The effect of pH was studied in the range 5.0–7.0 using model aqueous solutions of 50 ml volume and analyte concentration $0.2 \mu\text{g ml}^{-1}$ for nickel, cobalt and copper, $0.1 \mu\text{g ml}^{-1}$ for cadmium and $0.5 \mu\text{g ml}^{-1}$ for palladium. The obtained results are presented in Fig. 1. As can be seen, all analyte elements are quantitatively recovered (>95%) in the pH range 6–6.5.

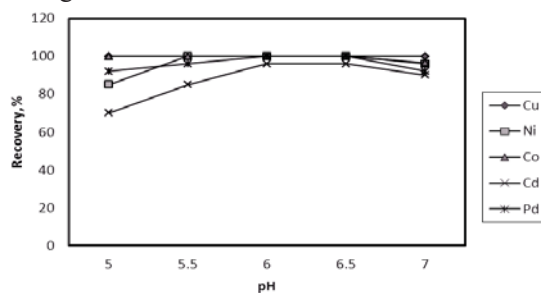


Fig. 1. Effect of pH on the recovery of Ni, Co, Cu, Cd and Pd with 2-nitroso-1-naphthol.

Effect of sample volume and amount of 2-nitroso-1-naphthol

The effect of sample volume on the recovery of the analyte elements was studied in the range from 20 to 250 ml. The results are shown in Fig. 2. As can be seen, the maximum sample volume allowing quantitative recovery of the analytes (>95%) is 160 ml. At higher sample volumes the recovery gradually decreases. For the quantitative preconcentration of nickel and cobalt sample volumes up to 200 ml were admissible.

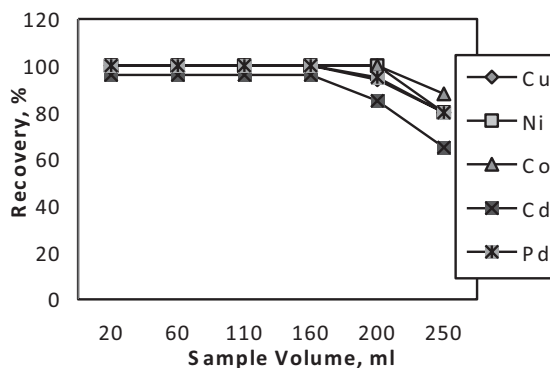


Fig. 2. Effect of sample volume on the recovery of Ni, Co, Cu, Cd and Pd with 2-nitroso-1-naphthol.

The amount of 2-nitroso-1-naphthol needed for the quantitative precipitation of the analyte elements at a 150 ml sample volume was optimized using increasing volumes of the 1% ethanolic 2-nitroso-1-naphthol solution. It was found that 10-12 ml was the optimal volume range of the reagent solution.

Effect of time of complexation

The effect of the time of complexation was studied over the range 15-60 min, see Fig. 3. As can be seen, the optimum time of complexation is 40 min. Longer time did not affect the recovery of the analytes.

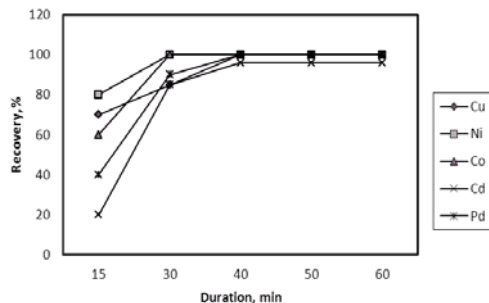


Fig. 3. Effect of time of complexation on the recovery of Ni, Co, Cu, Cd and Pd with 2-nitroso-1-naphthol

Interference studies

The precipitation of the analyte elements was studied in the presence of Na, K, Ca, Mg, Pb, Fe, Mn and Zn as possible matrix components (Table 1). No essential effects at the examined interferent levels on the recovery of the analytes were registered. The only exception was Cd with recoveries lower than 95%. Therefore, the standard addition method was adopted for Cd determination in further experiments.

Table 1. Effect of interferents on the determination of Cu, Ni, Co, Cd and Pd at the $\mu\text{g l}^{-1}$ level

Interferent	Concentration, mg l^{-1}	Recovery, %				
		Cu	Ni	Co	Cd	Pd
Na	100	99±2	99±2	100±2	83±2	99±2
K	10	99±2	99±2	99±2	90±2	99±2
Ca	6	100±2	99±2	99±2	91±2	99±2
Mg	6	99±2	99±2	99±2	91±2	99±2
Pb	2	98±2	98±2	98±2	84±2	98±2
Fe	5	98±2	98±2	98±2	80±2	98±2
Mn	2	99±2	100±2	100±2	83±2	99±2
Zn	3	101±2	100±2	100±2	91±2	99±2

Analytical parameters

The detection limits (DL) were calculated as 3σ of the blank signals: Co - $0.64 \mu\text{g l}^{-1}$, Ni - $0.61 \mu\text{g l}^{-1}$, Cu - $0.89 \mu\text{g l}^{-1}$, Cd - $0.10 \mu\text{g l}^{-1}$ and Pd - $0.60 \mu\text{g l}^{-1}$. The precision of the results was characterized by an RSD of 1.5-2.0%.

The accuracy of the method was checked by analysis of the reference material SPS-WW2 (waste water). As the RM does not contain Pd, the “added-found” method was used. The recovery of the added concentrations of Pd (0.167 and 0.067 mg l^{-1}) was 98 and 103%, respectively. In order to check whether the concentrations of the analytes determined by the present method are undistinguishable from the certified values Welch’s

Table 2. Measured ($n = 5$) and certified concentrations and t-statistic

	Ni	Co	Cu	Cd
Measured concentration, ng ml^{-1}	4945±65	300,8±4,4	1985±25	99,3±1,7
Certified concentration, ng ml^{-1}	5000±25	300±2	2000±10	100±0.5
t calc	1,70	0,35	1,19	0,84
V_{eff}^*	6,22	7,17	6,42	5,27
t (0,05; V_{eff})	2,45	2,36	2,45	2,57

* effective degrees of freedom

t-statistic evaluation was carried out according to [16]. The results obtained are shown in Table 2. As it can be seen, the values of t_{calc} are lower than the corresponding tabulated values at a probability of 0.05 and the corresponding effective degrees of freedom (V_{eff}) for all analytes which points to the good accuracy of the results and confirm the validity of the proposed method.

Application

The method was applied to the determination of traces of Cu, Ni, Co, Cd and Pd in capture water from

Table 3. Determination of Cu, Co, Ni, Cd and Pd in capture water from the region of an old copper mine (Bov, Bulgaria) and waste water from the copper plant “Assarel”, Bulgaria

Element	Capture water		Waste water	
	Concentration, mg l^{-1}	$u(c)$, mg l^{-1}	Concentration, mg l^{-1}	$u(c)$, mg l^{-1}
Ni	0.0068	0.00102	0.0350	0.00092
Co	0.0144	0.00097	0.0230	0.00093
Cu	0.0810	0.00378	0.4500	0.02529
Cd	0.0020	0.00007	0.0084	0.00023
Pd	< DL	-	< DL	-

a region close to an old copper mine (Bov, Bulgaria) and waste water from the copper-dressing plant "Assarel" in Bulgaria. The obtained results are shown in Table 3.

The results are given with their uncertainties. As can be seen, copper is the trace element with the highest content not only in the waste water sample, but also in the capture water sample. The latter may be attributed to the high residual level of this element in the environment of the former copper mine. The Pd content was below the DL of the method. It follows from the obtained results that the flame AAS determination of micro trace amounts of Co, Ni, Cu, and Cd in waters after precipitation of their complexes with 2-nitroso-1-naphthol is applicable to the analysis of real water samples.

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ПЛАМЪКОВО ААС ОПРЕДЕЛЯНЕ НА СЛЕДИ ОТ Cu, Ni, Co, Cd И Pd ВЪВ ВОДИ СЛЕД
КОНЦЕНТРИРАНЕ С 2-НИТРОЗО-1-НАФТОЛ

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Пламъкова ААС е използвана за определяне на следи от Co, Ni, Cu, Cd и Pd във води след утаяване на техни комплекси с 2-нитрозо-1-нафтол. Получената утайка е отделена от разтвора на пробата чрез филтруване през мембранен филтър с размер на порите 0.22 μm . Разтворена е в 5 ml етанол и е анализирана с помощта на пламъкова ААС. Границите на откриване за Co, Ni, Cu, Cd и Pd са съответно 0.61, 0.64, 0.89, 0.10 и 0.60 $\mu\text{g l}^{-1}$. Методът е валидиран с използване на референтен материал SPS-WW2 – Spectrapure Standards, Норвегия и е приложен за анализ на каптажна и отпадна вода.