Cloud Point Extraction as Sample Preparation Procedure Prior to Multielemental Analysis by Inductively Coupled Plasma-Optical Emission Spectrometry

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Extraction procedure based on cloud point phenomenon has been developed for simultaneous determination of Cd, Co, Cu, Fe, Mn, Ni and Zn in liquid samples by inductively coupled plasma optical emission spectrometry (ICP–OES). Complexes of metal ions with 1-(2-pyridylazo)-2-naphthol (PAN) were extracted from aqueous solutions into the surfactant-rich phase of octyloxypropylpolyethoxyethanol (Triton X–114) upon increase of the solution temperature. Factors affecting cloud point extraction, such as pH and concentrations of chelating agent and surfactant, were optimized. The highest extraction efficiencies for the studied analytes were obtained at pH = 9, Triton X–114 concentration of 0.25% (m/v) and at 5:1 molar excess of PAN over metal ions. Matrix effects caused by the presence of calcium and organic compounds in the analyzed solutions were investigated. Applicability of the optimized cloud point extraction procedure has been exemplary shown for tap and river water analysis by ICP–OES.


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The importance of micellar media in analytical atomic spectrometry is progressively increasing from year to year. Micellar media are used mainly in sample preparation step in spectrochemical analysis, although surfactants serve also for stabilization of slurries or modification of chemical reactions in order to generate volatile species, such as hydrides or alkylcompounds of metals or metalloids. The main field of interest in the last decade is preconcentration and/or separation of analytes using cloud point extraction (CPE) procedure. CPE is based on the phenomenon of phase separation of certain surfactant micelles in aqueous solutions upon temperature changes. Generally, the CPE procedure leads to high preconcentration factors and decrease in detection limits by one to two orders of magnitude. More detailed description of this procedure together with the factors influencing the micellization process can be found in some review papers dealing with the surfactant-mediated phase separation applications [1–6]. In preconcentration/separation step of metal ions prior to analysis by atomic spectroscopy techniques, solubilization of hydrophobic complexes in micelles of nonionic surfactants is mainly exploited. Some other phenomena, such as e.g. formation of a complex between surfactant and some cations are also employed [7–9].

Most of the papers dealing with CPE focus on preconcentration of one or two metal ions from liquid samples (water, parenteral solutions, saliva, urine, wine) [6–15] with the use of spectrophotometry [10, 11], atomic absorption spectrometry (AAS) [12, 13] and inductively coupled plasma–optical emission spectrometry (ICP–OES) [14, 15] as detection techniques. Three metallic species have been determined simultaneously in water and urine [16], digested blood [17] and water and wine [18] after extraction of various hydrophobic complexes into micellar phase of Triton X–114 followed by AAS analysis. Papers describing CPE for simultaneous multielemental analysis are relatively rare, although non-specific agents such as carboxylate, phosphate, pyridylazo or quinoline derivatives have been often used for the formation of insoluble complexes. This can be related to the necessity of finding the optimum experimental conditions to achieve good reproducibility, high preconcentration/separation efficiency and signal response for all analytes. In the case of multielemental analysis this problem may be complex and intricate due to specific limitation of complexation and extraction of metallic species as well as due to the necessity of optimization of the measurement parameters. Multielemental preconcentration procedures based on cloud point phenomenon have been developed for water analysis with AAS as a detection technique [19–23]. Application of CPE after formation of complexes with 1-(2-thiazolylazo)-2-naphthol (TAN) and later FAAS analysis for simultaneous preconcentration and determination of Cd, Cu, Pb and Zn in tap, river and sea waters has been reported [19]. A method based on CPE using ammonium pyrrolidinedithiocarbamate (APDC) and Triton X–114 as chelating agent and extraction medium,
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respectively, has been employed for determination of several (6–9) metallic species in natural waters by FAAS [20–22] and electrothermal AAS [23]. Application of ICP spectrometry for detection in multielemental analysis coupled with CPE sample preparation procedure is very seldom so far [24–26]. Inductively coupled plasma mass spectrometry (ICP–MS) with flow injection system has been used for the determination of several elements in water [24], while electrothermal vaporization coupled with ICP–MS has been exploited for determination of noble metals in urine and hair samples [25] after CPE. ICP–OES as a detection technique following CPE for preconcentration or separation of one or two metal ions has been performed in connection with flow injection systems [7, 14, 15, 27, 28]. Recently, a procedure based on CPE for simultaneous determination of Cd, Cr, Cu, Mn, Ni and Pb in saline oil refinery effluents and digested vegetable sample using ICP–OES has been reported [26]. Recoveries of the metals were between 90 and 111%.

This work has been undertaken in order to investigate the application of ICP–OES to the simultaneous multielemental analysis of liquid samples subjected to CPE preconcentration/separation procedure. The purpose was to optimize the CPE procedure using PAN as a chelating agent and Triton X–114 as a non-ionic surfactant, as well to study matrix effects and ICP robustness during introduction of the liquids with surfactants.

EXPERIMENTAL

Instrumentation

A JY38S inductively coupled plasma sequential spectrometer was used for the determination of analytes concentrations. Plasma operating conditions were as follows: 1.2 kW of rf power, 15 L min
$^{-1}$ of plasma Ar flow, 0.2 L min
$^{-1}$ of sheath gas flow and 0.3 L min
$^{-1}$ of carrier gas flow. The samples were introduced into the plasma using a Meinhard nebulizer in a cyclonic chamber. The most sensitive lines: Cu I (324.7 nm), Cd II (228.8 nm), Co II (228.6 nm), Ni II (221.6 nm), Mn II (259.4 nm), Zn II (202.5 nm), Fe II (259.9 nm) were measured. A MPW–350 centrifuge (Med. Instruments) was used for separation of micellar and aqueous phases. A CP–401 pH-meter (Elmetron) with a combined glass electrode was used for pH measurements.

Reagents, solutions and samples

All reagents were of analytical or higher grade. Deionized water (18.3 MΩ cm
$^{-1}$, Barnstead Pure$^\text{TM}$) was used for preparation of the solutions. Working solutions containing metal ions were prepared from 1000 mg L
$^{-1}$ one-element stock solutions. Water samples were filtered to remove the suspended solids, acidified with HCl and stored in a refrigerator until analysis. Multielement standard solution (Merck ICP standard solution IV) was used for the preparation of the working standards. A 0.5% (m/v) solution of 1-(2-pyridylazo)-2-naphthol (PAN) in ethanol (POCh, Poland), a 10% (m/v) solution of Triton X–114 (Fluka) and ammonia buffer solution (pH = 9.0) were used for extraction. A 20 g L
$^{-1}$ Ca solution was prepared from
calcium nitrate (POCh, Poland). Laboratory glassware was cleaned in 10% HNO₃ in an ultrasonic bath and then rinsed with deionized water.

Cloud point extraction procedure

20.00 mL of sample solution containing metal ions at concentration 100 mg L⁻¹ were placed in a tube. Then, 1 mL of buffer solution, 0.1–0.5 mL of Triton X–114 and 50–200 mL of PAN solution were added and the tube was placed for 15 min in a water bath at 50°C. Separation of the micellar phase from the aqueous phase was performed by centrifugation of the solution for 10 min at 4000 rpm. The tube was then placed in an ice bath for 10 min. The aqueous phase was removed by simply inverting the tube. In order to decrease viscosity, 100 mL of ethanol and 1 mL of HNO₃ (1:1) were added to the organic phase, the solution was transferred to the flask and its volume was made up to 10.0 mL with deionized water. Blank samples were subjected to the same procedure in parallel to the samples.

RESULTS AND DISCUSSION

Optimization of CPE procedure

Among variables affecting extraction efficiency, three parameters: pH, PAN concentration, and surfactant concentration were consecutively optimized to find the best conditions for CPE. Other parameters, i.e. equilibration time, incubation temperature and centrifugation conditions were selected according to the literature reports [13, 16, 29–31].

Formation of stable hydrophobic complexes of metal ions with PAN as a chelating agent is strongly affected by pH of the solution. Cloud point preconcentration of Co in urine was performed at pH 3.7 [29]. In capillary electrophoresis after CPE preconcentration of Co and Cu ions using PAN the optimal pH was 8.5 [30], while in spectrophotometric determination of Co, Ni and Zn in water and urine samples pH 9.2 was applied [16]. In order to determine the optimum pH for CPE procedure in our study, solutions containing metal ions were subjected to extraction within the pH range 4–9.5. In Figure 1 the effect of pH on relative intensities of Ni, Co, Cu and Cd lines is presented. Mean relative standard deviations (RSD) were 5.3%, 3.9%, 2.4% and 2.7% for Ni, Co, Cd and Cu, respectively. The Co line intensities were almost constant in the pH range from 4.8 to 9.0, taking into account RSD values. For Ni and Cu the optimum pH range was: 5.5–9.5, but for Cd the highest signals were observed at pH > 7.5. For further simultaneous extraction of all metal ions pH 9.0 was selected.
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Different excess of PAN in relation to metal ion was used to achieve quantitative complexation and high efficiency of the CPE process [13, 16, 30, 31]. The effect of PAN concentration in the range $2.0 \times 10^{-4}$ to $1.4 \times 10^{-3}$% (m/v) on extraction efficiency is presented in Figure 2. Analytical signals of Co, Cu and Ni were practically independent of PAN concentration, only the Cd line intensity at the lowest chelating agent concentration was diminished by 20%. Quantitative formation of complexes was observed for PAN-to-metal ion ratios larger than 4:1. For simultaneous extraction of metal ions from multielement solutions PAN content was kept at a 5-fold or higher molar excess over the total content of all metal ions.

In inorganic applications of CPE, various Triton X–114 concentrations ranging from 0.03% [26] to 1% [14] were used as optimum. Here, the effect of surfactant concentration on extraction efficiency was studied for solutions containing several metal ions forming stable complexes with PAN in alkaline medium. In Figure 3 the changes of relative line intensities vs surfactant concentration are presented. The intensities increased with the Triton X–114 concentration increase up to 0.25% (v/v). At higher concentrations extraction efficiency remained constant. Only for manganese the intensity decreased by about 10% at surfactant concentrations higher than 0.25%. High extraction efficiencies show that the CPE procedure conducted at pH = 9.0, Triton X-114 concentration of 0.25–0.30% (m/v) and five-fold molar excess of PAN can be applied for simultaneous separation and/or preconcentration of Cd, Co, Cu, Fe, Mn, Ni and Zn ions.

Figure 1. Dependence of relative line intensities on pH ($c_{\text{Trit}} = 0.2\%$, $c_{\text{PAN}} = 2.0 \times 10^{-4}\%$)
Figure 2. Effect of PAN concentration on relative line intensities (pH = 9.0, \(c_{\text{TX114}} = 0.2\%\)). Error bars represent standard deviations (n = 5).

Figure 3. Effect of Triton X–114 concentration on relative line intensities (pH = 9.0, \(c_{\text{PAN}} = 1.0 \times 10^{-3}\%\)). Error bars represent standard deviations (n = 5). (Continuation on the next page)
Specificity of ICP–OES, *i.e.* relatively high solution volume requirements for multielemental analysis, causes that the obtained preconcentration factors, due to the CPE procedure, are not so impressive as in case of such methods as AAS. However, higher preconcentration factors can be achieved by increasing the volume of the initial sample or using other sample introduction systems *e.g.* micronebulizers or direct injection nebulizers.

**Effect of organic matrix**

Solutions obtained after the CPE procedure contain relatively large amounts of organic compounds (EtOH, surfactant), which can change plasma parameters and emission intensities [32]. The influence of individual organic additives as well as their mixtures on emission intensity of multielemental solutions was studied. The results are presented in Figure 4 as a ratio of the intensity measured for the solution containing EtOH and/or Triton X–114 to the intensity measured for the aqueous standard solution of the same concentration of metal ion. The concentrations of organic species were the same as in final solutions obtained after extraction. Generally, an addition of EtOH increased emission signals by up to 18%, depending on the element. The presence of Triton X–114 in the samples, as observed earlier [33], did not change (or caused a slight suppression of) the analytical signals, even at relatively high surfactant concentration. The effects caused by the mixture of both organic compounds were similar to the effect of ethanol.
In order to monitor the plasma response to the changes in its chemical composition, the Mg II 280.270/Mg I 285.213 nm intensity ratio was investigated. In case of radial plasma observation, the Mg II/Mg I ratio above 8 indicate the so-called robust conditions and resistivity of the plasma to matrix effects. In our experiments the Mg II/Mg I intensity ratio during aspiration of aqueous solutions into the plasma was about 10.3. For aqueous-organic solutions the Mg II/Mg I intensity ratio increased to about 11.3–11.5, what could be related to the higher increase of ionic than atomic line intensities for solutions containing ethanol [34].

**Effect of calcium matrix**

A great number of samples analysed by ICP spectrometry are of biological origin and contain considerable amounts of alkaline or alkaline earth elements. These elements introduced into plasma can change both plasma parameters as well as analytical signals. As it results from our earlier study [35], the presence of calcium in a sample solution causes a significant decrease in line intensities by 20–30%. Severe matrix effects and plasma instabilities can be avoided by efficient separation of trace elements from the calcium matrix. Therefore, it seemed worthwhile to check if the CPE procedure could serve for separation of the analytes from solutions of high calcium concentration. In Figure 5 the recoveries for Co, Cd, Cu and Ni after CPE procedure carried out for the solutions containing different Ca concentrations are presented. The RSD values did not exceed 4%. The quantitative recoveries for analyte-to-calcium mass ratios reached up to 1 : 20000. At the highest Ca concentration...
the recoveries were ca 90%. In the final solutions, the content of Ca was below 8% of the initial content. These results have shown that the CPE procedure might be very useful for separation of trace metal ions from calcium-rich solutions, what allows one to reduce deterioration of the analytical signals as well as to decrease the Ca-related background.

![Figure 5](image-url) Effect of calcium matrix on recoveries of Co, Cu, Cd, and Ni (c_{TXH} = 0.25%, c_{EtOH} = 1%, c_{PAN} = 1.0 \times 10^{-3}%)  

Application to water analysis

The proposed method has been applied to determination of several elements in tap and river waters. Water samples were subjected to the CPE procedure under the optimized conditions. In addition, recovery experiments were carried out by spiking the samples with different amounts of Cu, Cd, Ni, Mn and Co before extraction. Each sample was analyzed five times. Quantification was performed using matrix matching standards. The obtained results are presented in Table 1. The recoveries for the samples with various additions of metal ions ranged from 93 to 110%. Concentrations of Fe and Zn in water samples were measured before and after CPE. Before CPE, the concentrations of Zn and Fe in tap water were 0.346 ± 0.015 mg mL$^{-1}$ (Zn) and 0.188 ± 0.006 mg mL$^{-1}$ (Fe), and after CPE they equaled 0.338 ± 0.019 mg mL$^{-1}$ and 0.186 ± 0.005 mg mL$^{-1}$ for Zn and Fe, respectively. For river water the recoveries were 110% for Zn and 104% for Fe.
Table 1. Results of determination of trace elements in tap and river waters

<table>
<thead>
<tr>
<th>Element</th>
<th>Added, ng mL(^{-1})</th>
<th>Found(^a), ng mL(^{-1})</th>
<th>Recovery, %</th>
<th>Added, ng mL(^{-1})</th>
<th>Found(^a), ng mL(^{-1})</th>
<th>Recovery, %</th>
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<td>River water</td>
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<td>Tap water</td>
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<td>Cu</td>
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<td>38 ± 12</td>
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<td></td>
<td>50</td>
<td>322 ± 10</td>
<td>97.9</td>
<td>50</td>
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<td>–</td>
<td>nd(^b)</td>
<td>–</td>
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<tr>
<td></td>
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<tr>
<td>Co</td>
<td>–</td>
<td>nd(^b)</td>
<td>–</td>
<td>nd(^b)</td>
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<td>–</td>
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\(^a\) Mean ± standard deviation, n = 5.

\(^b\) Not detectable.
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CONCLUSIONS

Cloud point extraction using PAN and Triton X–114 has been found an effective sample pretreatment procedure for multielemental analysis of liquid samples by ICP–OES. Under optimized conditions, the complexes of metals with PAN were sufficiently stable to ensure quantitative extraction and simultaneous determination of Cd, Cu, Co, Ni, Mn, Zn and Fe. Matrix effects caused by the presence of organic compounds in the measured solutions were insignificant and caused mainly by ethanol. The proposed method has been successfully applied to the separation of the analytes from the calcium matrix as well as for trace analysis of real water samples. Quantitative recoveries and good reproducibility for seven elements in tap and river waters were achieved.

REFERENCES


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