



CO-PRECIPIATION AS A SAMPLE PREPARATION TECHNIQUE FOR TRACE ELEMENT ANALYSIS: AN OVERVIEW

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ABSTRACT

Sample preparation is an important step in chemical analysis process. The present article gives an overview about the co-precipitation as a technique for sample preparation for trace element analysis. Co-precipitation steps, mechanism, advantages, disadvantages and some applications have been discussed.

Key words: Co-precipitation, Sample preparation, Separation, Pre-concentration.

INTRODUCTION

Sample preparation was probably the single most neglected area in analytical chemistry relatively to the great interest in instruments. While the level of sophistication of the instrumentation for analysis has increased significantly, a comparatively low technical basis of sample preparation often remains¹.

The principal objectives of sample preparation for residue analysis are; isolation of the analytes of interest from as many interfering compounds as possible, dissolution of the analytes in a suitable solvent and pre-concentration. In an analytical method, sample preparation is followed by a separation and detection procedure. The selection of a sample preparation method is dependent upon: (1) the analyte(s), (2) the analyte concentration level(s), (3) the sample matrix, (4) the instrumental measurement technique, and (5) the required sample size².

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emission or inductively coupled plasma mass spectrometry is not always possible due to matrix interferences and the very low concentrations of metal ions. Therefore, a pre-concentration/separation step is required. To accomplish this task a solvent extraction, co-precipitation, cloud point extraction technique can be applied^{3,4}. Solid phase extraction was used to separate and preconcentrate metal ions for analytical purposes⁵. Modified silica gels was also applied for the preconcentration of trace elements⁶. Adsorption and nanofiltration techniques has also been applied for heavy metals preconcentration⁷.

Some of these methods suffer from inconveniences such as, lengthy separation, limitation of the volume of sample solution investigated, time consuming, multi stage, lower enrichment factor and consumption of organic harmful solvents⁸.

Co-precipitation methods may overcome some limitations of the other method of extractions due to the different mechanism of extraction.

RESULTS AND DISCUSSION

The pre-concentration purpose is achieved by the formation of insoluble compounds. The co-precipitation is used when direct precipitation cannot separate the desired metallic species due to its low concentration in sample solution. The co-precipitation can be associated with metal adsorption on the precipitate surface or due to metal incorporation onto the precipitate structures.

Inorganic or organic substances can be used as co-precipitation agents. The organic agents usually chosen are those able to originate neutral chelates with metallic species. The carrier element, is precipitated to co-precipitate trace elements in sample solutions, copper and zinc are popular, because of their limited negative effects on environment.

After precipitation the precipitate can be removed by centrifugation and filtration or decantation and then dissolved in acids or in an organic solvent, such as isobutyl methyl ketone to be measured^{9,10}.

Co-precipitation using hydroxides as the carrier of trace elements is the most often used one in inorganic coprecipitation, for example $\text{Fe}(\text{OH})_3$, $\text{Mn}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, $\text{La}(\text{OH})_3$, $\text{Zr}(\text{OH})_3$, $\text{Th}(\text{OH})_3$, $\text{Mg}(\text{OH})_2$, and $\text{Ni}(\text{OH})_2$. This is because the hydroxides of most metals are insoluble in neutral pH solutions, which indicate that the hydroxide carriers can pre-concentrate most metals. The other reason is that anion matrix is not generated from the carrier after dissolution of hydroxides with an acid solution, which benefit the measurement of trace elements.

Chelating agents (NaDDC, APDC, dithiozone) in combination with metals, such as cobalt, metal hydroxides (cerium, magnesium and iron hydroxides) or water soluble polymers (polyacrylamide, polyacrylic acid and polyvinylpyrrolidinone) are often used as co-precipitants¹¹⁻¹⁴.

In organic precipitation, trace elements are collected as metal complex with organic reagents, which usually have better selectivity for metals ion than inorganic reagents. The course of reaction can be controlled by changing pH values and concentration of the complexing agents, by introducing masking agents, and by the formation of mixed complexes which gives the possibility for almost any ion entering the complexing reaction to be separated. The organic reagents, which may cause interferences with the measurements of trace elements, in the pre-concentrated sample can be removed by combustion.

From physical point of view, there are three principal mechanisms in co-precipitation process:

Surface adsorption: The surface charge on the precipitate can attract ions in solution of the opposite charge.

Inclusion: The analyte may isomorphically replace an ion in the crystal structure of the precipitate (mixed crystal), or be incorporated non-isomorphically (solid solution).

Occlusion: Ions are physically engulfed in the forming precipitate before they can diffuse or be carried away.

Co-precipitation can be highly efficient, and a wide range of analytes can be collected, but there are major disadvantages. The precipitate, which has a mass of many orders of magnitude greater than that of the analyte, can be a major source of contamination. The removal of the analyte from the precipitate matrix may require further separation, with associated losses and blanks. There is also possible contamination and loss in all handling steps, such as filtration and dissolution of the precipitate. The total amounts of trace elements in the sample solution can be determined by using the carrier element as an internal standard element, because the loss of trace elements is generally proportional to that of the carrier element^{15,16}.

Some of these problems can be negated by the use of organic reagents to complex and then to precipitate the analytes. The organic reagent is normally added in water-soluble volatile solvent to an aqueous sample, and if precipitation of the organic complexant does

not occur spontaneously, the organic solvent can be removed by heating to initiate precipitation.

Despite the limitations, inorganic precipitates have been used in many applications. Iron co-precipitation can be employed for example for the concentration of rare earth elements from sea water at ng L^{-1} concentrations.

Many metal ions from water samples have been pre-concentrated by co-precipitation with hydroxides of iron (III)¹⁷, indium (III)¹⁸, and zirconium¹⁹. Organic co-precipitants, generally dithiocarbamates of bismuth and copper have been widely used as efficient collectors of trace elements^{20,21}. A separation/pre-concentration procedure based on the co-precipitation of Pb(II), Fe(III), Co(II), Cr(III) and Zn (II) ions with copper(II)-N-benzoyl-N-phenyl-hydroxylamine complex (Cu BPHA) has been also developed^{22,23}.

Ni(II)/2-Nitroso-1-naphthol-4-sulfonic acid precipitate was used for the coprecipitation of Co, Pb, Cu, Fe and Zn prior to their flame atomic absorption spectrometric (FAAS) determinations in environmental samples. The precipitate could be easily dissolved with concentrated nitric acid. The recovery values for analyte ions were higher than 95%²⁴.

Armagan et al.²⁵ have used the co-precipitation technique for separation and pre-concentration of gold(III), bismuth(III), cobalt(II), chromium(III), iron(III), manganese(II), nickel(II), lead(II), thorium(IV) and uranium(VI) ions by the aid of Cu(II)-9-phenyl-3-fluorone precipitate. The Cu(II)-9-phenyl-3-fluorone precipitate was dissolved by the addition 1.0 mL of concentrated HNO_3 and then the solution was completed to 5 mL with distilled water. Iron, lead, cobalt, chromium, manganese and nickel levels in the final solution were determined by flame atomic absorption spectrometer, while gold, bismuth, uranium and thorium were determined by inductively coupled plasma mass spectrometer. The pre-concentration factor was 30, and gold(III), bismuth(III), chromium(III), iron(III), lead(II) and thorium(IV) were quantitatively recovered from the real samples.

Sherrod et al.²⁶ have suggested a rapid separation method that allows separation and pre-concentration of actinides in urine samples was developed for the measurement of longer lived actinides by inductively coupled plasma mass spectrometry (ICP-MS) and short-lived actinides by alpha spectrometry. Pre-concentration was performed using a streamlined calcium phosphate precipitation. The chemical recoveries are typically greater than 90%. This method allows measurement of both long-lived and short-lived actinide isotopes. ^{239}Pu , ^{242}Pu , ^{237}Np , ^{243}Am , ^{234}U , ^{235}U and ^{238}U were measured by ICP-MS, while ^{236}Pu , ^{238}Pu , ^{239}Pu , ^{241}Am , ^{243}Am and ^{244}Cm were measured by alpha spectrometry.

A sensitive and accurate method for the determination of chromium at the ultra-trace levels has been determined in river water and sea water by GFAAS. Chromium was pre-concentrated by co-precipitation with a combination of 8-quinolinol, palladium as a carrier element and tannic acid as an auxiliary complexing agent, and the co-precipitates obtained were directly measured by graphite furnace atomic absorption spectrometry (GFAAS) using the solid sampling technique. Chromium is co-precipitated quantitatively with Pd/8-quinolinol/tannic acid complex in the pH range of 5.1–5.3²⁷.

Co-precipitation has also been combined with energy-dispersive X-ray fluorescence for the analysis of environmental water. Ti(IV), Cr(III), As(V), Pb(II) and Th(IV) have been co-precipitated on aluminum hydroxide with quantitative recoveries. The precision was 4-6% and the detection limits were in the range 0.2–0.8 $\mu\text{g L}^{-1}$.²⁸ Quantitative recoveries have also been obtained for Ni, Cu, Zn and Pb, on iron hydroxide at the 10 μgL^{-1} level in waters²⁹.

U and Th isotopes have been measured in soil samples by alpha-spectrometry after co-precipitation with LaF₃. The recoveries of chemical separation were rather high (about 80%), that leads to the use of a small weight of soil sample (about 0.5 g)³⁰.

CONCLUSION

Co-precipitation is a separation–pre-concentration technique based on phase separation. Analyte ions could be precipitated in the procedure with the combination of a carrier element and a suitable chelating agent. Some advantages of co-precipitation, as enrichment technique, are that pure inorganic reagents can be easily obtained and also the procedure is easily handled. High recoveries and high pre-concentration factors can be achieved by co-precipitation.

REFERENCES

1. Dean, Atomic Absorption and Plasma Spectroscopy, John Wiley and Sons, Ltd., Chichester (1997).
2. N. R. Bader, An Overview, *Rasayan J. Chem.*, **4**, 49 (2011).
3. A. R. Zarei and M. R. Sovizi, *J. Anal. Chem.-Engl. TR*, **66(3)**, 269 (2011).
4. I. Komjarova and R. Blust, *Analytica Chimica Acta* (2006) 576, 221.
5. A. L. Valfredo, S. G. T. Leonardo, B. Marcos de Almeida, C. S. C. Antonio, T. C. Jacira, A. M. C. Luiz, S. J. Djane, S. S. Elenir, X. B. Patrícia and N. S. Luana, *Appl. Spectr. Rev.*, **43(4)**, 303 (2008).

6. D. Kara and A. Fisher, *Sep. Purif. Rev.*, **41(4)**, 267 (2012).
7. N. Waldt, B. Wiedmann and J. V. Oostrum, *A Reviews – Sep. Purif. Rev.*, **41(3)**, 169 (2012).
8. H. A. Panahi, M. Karimi, E. Moniri and H. Soudi, *African J. Pure Appl. Chem.*, **2(10)**, 96 (2008).
9. Hengwu, C. Jincao, J. Yufeng, W., *Anal. Chim. Acta*, **353(2-3)**, 181 (1997).
10. S. Saraoglu, U. Diverikli, M. Solyak and L. Elci, *J. Food Drug Anal.*, **10**, 188 (2002).
11. J. F. Wu and E. A. Boyle, *Anal. Chem.*, **69**, 2464 (1997).
12. L. Elci, U. Sahin and S. Oztas, *Talanta*, **44**, 1017 (1997).
13. S. Saracoglu, M. Soylak and L. Elci, *Talanta*, **59**, 287 (2003).
14. N. Tokman, S. Akman and C. Ozeroglu, *Talanta*, **63**, 699 (2004).
15. S. Kagaya, S. Miwa, T. Toshiyuki Mizuno and K. Tohda, *Analytical Sciences*, **23**, 1021 (2007).
16. A. G. Howard, P. Stathm, *J. Inorganic Trace Analysis, Philosophy and Practice*, John Wiley & Sons Ltd. (1997).
17. Y. Kashiwagi and E. Kokufuta, *Anal. Sci.*, **16**, 1215 (2000).
18. M. Hiraide, Z. Chen and H. Kawaguchi, *Anal. Sci.*, **7** (1991).
19. Y. Tamari, R. Hirai, H. Tsuji and Y. Kusaka, *Anal. Sci.*, **3**, 313 (1987).
20. H. Sato, Ueda J. *Anal Sci.*, **17**, 461 (2001).
21. S. Tokalıoğlu, T. Oymak and S. Kartal, *Microchim Acta*, **159**, 133 (2007).
22. S. Saçmacı and S. Kartal, *Microchim Acta*, **170**, 75 (2010).
23. N. R. Bader, *An Overview Der Chemica Sinica*, **2**, 211 (2011).
24. O. D. Uluozlu, M. Tuzen, D. Mendil, M. Soylak, *J. Hazard. Mater.*, **15**, 176, 1032 (2010).
25. F. Armagan, A. B. Ayden and M. Soylak, *Talanta*, **73**, 134 (2007).
26. L. Sherrod, Maxwell and Vernon D. Jones, *Talanta*, **80**, 143 (2009).

27. Q. Zhang, H. Minami, S. Inoue and I. Atsuya, *Analytica Chimica Acta*, **401**, 277 (1999).
28. M. A. H. Eltayeb and R. E. Van Grieken, *Analytica Chimica Acta*, **268**, 177 (1992).
29. R. Chakravorty and R. Van Grieken, *Int. J. Environ. Analy. Chem.*, **11**, 67 (1982).
30. N. Q. Huy, T. T. Bich and N. V. Suc, *J. Radioanalyt. Nuclear Chem.*, **269**, 129 (2006).

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