Continuous Preconcentration of Sn^{2+}/Sn^{4+} by the On-line Sulfide Precipitation-Dissolution

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The technique of an on-line preconcentration by the direct sulfide precipitation has been developed. Sn was homogeneously precipitated by sulfide, which was generated *in situ* from the hydrolysis of thioaceteamide. Precipitate was collected on a filter in the line and dissolved out instantaneously by KOH to be sent to an ICP. The enrichment factor was 4 with the sampling speed of 15/hr for 1.0 mL of sample. It was increased to more than 40 times when the sampling volume was increased to 10 mL with the sampling speed of 5/hr. Sn^{2+}/Sn^{4+} could be separately determined with the on-line precipitation technique. The method was applied to the analysis of NIST SRM 1566 Oyster sample and yielded good agreement with the certified value.

Key Words : Preconcentration, Sn^{2+}/Sn^{4+} speciation, ICP, Sulfide precipitation

Introduction

Recently, the on-line precipitation preconcentration technique[1-7] has been developed and draws much interest since it can provide several advantages such as a high enrichment factor, matrix separation, speed, simplicity and automation. It is also attractive because that it is considerably less prone to contaminations than a batch type. Few glasswares are used and samples are contained in a closed line separated from the environment. Furthermore, small quantities of samples can be treated and analyzed. Most studies of the continuous precipitation technique have been using coprecipitation[6-9] because it is very effective in collecting trace amount of sample ions. Both inorganic[10,11] and organic[12,13] carriers were used. However, the coprecipitation technique has a limited enrichment factor because the large amount of precipitates generated can hinder or even stop the flow. Consequently, Weltz *et al*.[10] used a filterless collector such as a "knotted reactor" to increase sample throughput. However, it took a long time to dissolve the precipitates. Consequently, the signal peak shape became broad and the sensitivity was decreased.

Direct precipitation technique has advantages because it does not need to collect a large amount of additional carrier precipitates. Thus, a large sample can be employed for a higher enrichment factor and the collected precipitates can be dissolved in a short time producing a sharp and narrow peak. Cd[6] and As[7] were analyzed with the direct precipitation preconcentration technique using sulfide and hydroxide as a precipitant, respectively. An organic precipitating reagent could also be used also and applied to the analysis of Co.[12] In principle, any precipitants that are able to form a precipitate can be chosen to collect sample ions. In addition to preconcentration, importantly, the direct precipitation technique can be applied to the speciation study as shown in this work.

Sulfide precipitates are divided into Copper group (2A), Tin group (2B), Iron group (3A), and Aluminum group (3B). All the groups can be preconcentrated by forming sulfide precipitates. Though the hydride generation technique can give a higher sensitivity, the continuous flow preconcentration technique is a very general and much more applicable to other ions that do not even form any volatile hydrides.

Sn is ubiquitous and has been widely used in metallurgy, food and clinical industry. It has been known to be relatively harmless and regarded as an innocuous background material. Though established as an essential element for humans, studies show that it may cause psychiatric abnormalities such as psychosis.[14] The increase in the use of tetrabutyltin-based paints in a ship industry called attention to the marine environment since 1970s.[15] Thus, it is important to measure not only the total quantity but each species of Sn.[16-18] In this report, the homogeneous precipitation in an on-line system, which is very unique, was employed. In our best knowledge, the on-line preconcentration with homogeneous precipitation has been introduced by our group first. Tin is easily precipitated with sulfide that is generated from thioaceteamide *in situ*. Furthermore, the on-line precipitation-dissolution system could be applied to the separation of Sn^{2+} and Sn^{4+} by selecting proper experimental conditions. The work can be easily extended to other elements in the sulfide-precipitating group such as Pb, Hg, Bi, Cd, and Sb.

Experimental Section

Experimental Apparatus and Reagent. The experimental design is shown in Figure 1. Detailed description is avoided and only a schematic diagram is shown. For detection of Sn, Inductively Coupled Plasma (ICP) used in this experiment was model ICP 1000 (Perkin Elmer, New Jersy, USA) and the optimum running conditions are listed in Table 1. The sample was injected using a 6-way injection valve (Rheodyne,

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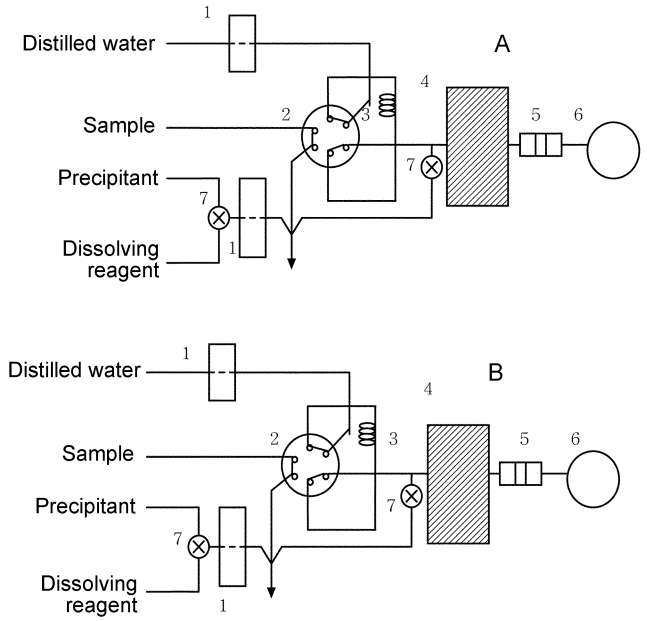

Figure 1. A Schematic diagram of the continuous precipitation preconcentration system. A; "load", B; "inject" position 1: peristaltic pump 2: injection valve 3: sample loop 4: reaction coil immersed in a water bath 5: filter 6: ICP 7: valve.

Table 1. A Typical Experimental Operating Condition of ICP Used in the Experiment

R. F. Power	:	1.0 kW
Nebulizer Gas Flow	:	1.0 L/min
Auxiliary Gas Flow	:	1.0 L/min
Plasma Gas Flow	:	15 L/min
Viewing Height	:	15 mm
PMT Voltage	:	600 V
Wavelength	:	Sn(I) 286.1 nm

CA, USA). All the line employed was 1.0 mm i.d. PTFE (Polytetrafluorethylene). Basic experimental system was the same as the one used before.[5]

All water used was doubly distilled from the Milli-Q water system (Millipore, Bedford, MA, USA). The standard solution of Sn was made from pure Sn metal (99.999%, Alfa Prod. Danvers, MA, USA). To ensure the Sn^{4+} sample is in the same chemical state, it was oxidized with H_2O_2. Extra amount of H_2O_2 was removed by boiling the solution. For a homogeneous precipitation, thioaceteamide was hydrolyzed at an elevated temperature and H_2S was generated in solution. Saturated thioaceteamide solution was prepared by dissolving 16.3 g of thioaceteamide in 100 mL.

Procedure. In "load" position, a sample was loaded while the system was being rinsed by the water. The sampling loop size could be varied from 0.1 mL to several mL or larger. A precipitant, sulfide or NH_4OH, was sent to be mixed with a sample through a T-connector, which was located just before the reaction coil. When the valve was in the "injection" position, sample was mixed with thioaceteamide to enter into the reaction coil. The temperature of the reaction coil was set at 70 °C to enhance the hydrolysis reaction of thioaceteamide. Precipitates were formed and collected on a filter. After 20 seconds of washing, a dissolving reagent (KOH or ammonium sulfide) was sent for 20 seconds. The system was rinsed with water for 10 seconds for the next run. The total time taken for a run normally took 4 minutes.

Results and Discussion

Generation and Dissolving of Precipitate. Sulfide precipitate was formed by S^{2-}, which was generated homogeneously from the hydrolysis of thioaceteamide. Both Sn^{2+} and Sn^{4+} could form sulfide precipitates readily when reacted with sulfide. H_2S should be treated with care because it is toxic. Its lethal dose is only 700 ppm. However, the sense of smell is getting soon tired and one is not able to smell anymore. Therefore, it is more advantageous to use thioaceteamide to generate a limited amount of H_2S than to use it directly. Another advantage of using thioaceteamide is that coprecipitation could be reduced by generating a proper amount of sulfide ions. Excess sulfide ions adsorbed on the surface of precipitates can easily coprecipitate other cations. Since the pH of the solution can be varied by the hydrolysis reaction, the pH should be fixed at 0.5 by adding an acid.

The dissolving reagent should be able to dissolve a precipitate quickly and completely. Since 2B elements are amphoteric, they can be dissolved in both acid and base. Ammonium sulfide and KOH dissolve tin precipitates into SnS^{3-}, and $Sn(OH)_6^{2}$, respectively.

$$3\ SnS_2\ (s) + 6\ OH^-(aq) \rightarrow [Sn(OH)_6]^{2-}(aq) + 2[SnS_3]^{2-}(aq)$$

or

$$SnS_2(s) + (NH_4)_2S(aq) \rightarrow [SnS_3]^{2-}(aq) + 2\ NH_4^+(aq)$$

If a precipitate is dissolved slowly, the peak shape would be broad and the sensitivity decreases. A sharp peak is more advantageous as it is in the chromatographic study. Thus, the most important factor is the ability to dissolve precipitates quickly. It was observed in the experiment that both ammonium sulfide and KOH could be used as well. However, ammonium sulfide dissolved the precipitates more slowly than KOH. In addition, the generation of ammonia in ICP has made the plasma unstable. In the experiment, 1.0 M KOH was found to be the most efficient for sulfide precipitate.

Reaction Time. The reaction time can be controlled either by varying the length of the reaction coil and/or the flow rate. The length of the reaction coil should be properly decided because a short one may not provide enough reaction time and consequently reduce the enrichment factor. On the other hand, a long one can reduce the sample throughput. Coil length was varied preferably while the flow rate was fixed at 0.95 mL min^{-1}. The length of coil was changed to 0.5 m, 2 m, and 4 m and the reaction time was calculated as 15 s, 60 s, 120 s, respectively.

The relationship between the reaction time and signal is shown in Figure 2. As expected, the signal increased with the reaction time and stayed constant after a minute. The

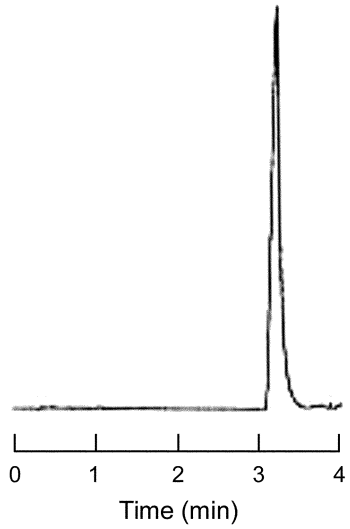

Figure 2. A typical peak obtained for Sn sulfide precipitation-dissolution. No baseline increase before the peak means the precipitation reaction is complete.

reaction between tin and precipitant was fast enough to be completed. The aging effect was also considered. When the reaction coil or the reaction time was too short, precipitates could be in a colloidal state thus easily passing through a filter. To examine the aging effect, aging time was given for more than 10 minutes by stopping the flow while the precipitate was staying in the reaction coil. Little change with aging revealed that the precipitation reaction was fast enough. The reaction coil length was limited to 3 or 4 meters long.

Temperature. Temperature was considered to be a very important parameter in producing good precipitates especially in the homogeneous precipitation using the hydrolysis of thioaceteamide. A constant temperature was kept by putting the reaction coil in a temperature controlled water bath. The signal was not increasing much after 35 °C. However, precision became better at higher temperature of 60 °C. When it was over 80 °C, there was not much change. Since the precipitate showed good stability below 70 °C, the experiment was performed at 70 °C or below. In the case of hydroxide precipitation, temperature control was not necessary.

Flow Rate of Thioaceteamide. The amount of thioaceteamide to sample was varied by changing the flow rate from 0.1 to 0.4 mL min^{-1} while the flow rate of sample was fixed at 0.75 mL min^{-1}. Nebulization was most efficient when the total flow rate was about 1.1 mL min^{-1}. The result is shown in Figure 3. For signal and stability, 0.3 mL min^{-1} was the best.

On-line Preconcentration. The optimum condition is summarized in Table 2. Using this condition, a typical result for Sn is shown in Figure 4. No baseline increase before the peak means that Sn formed sulfide precipitate well and completely filtered. The sharp peak suggests that the precipitate was dissolved out instantaneously.

Speciation Study of Sn^{2+}/Sn^{4+}. This study shows the feasibility for the separation between Sn^{2+} and Sn^{4+} with the

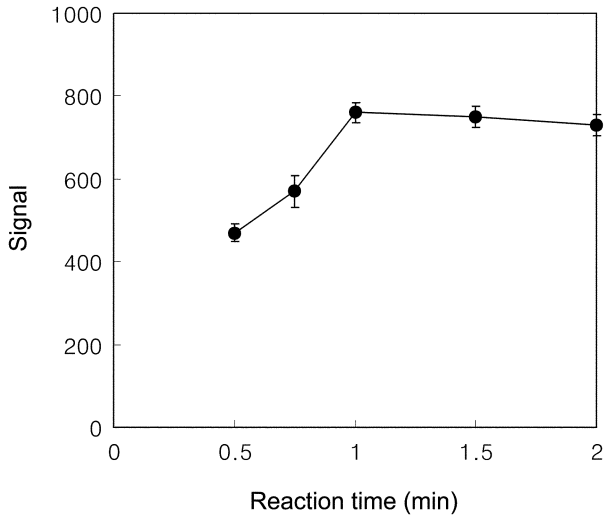

Figure 3. Signal as a function of the reaction time.

Table 2. The Optimum Experimental Condition of Continuous Preconcentration by a Direct Precipitation Technique

Flow rate	: 0.75 mL/min
Reaction coil length	: 4 m
Reaction Temperature	: 70 °C
Flow rate of precipitant	: 0.3 mL/min
Dissolving solution	: 1.0 M KOH
Filter type	: 0.45 μm membrane filter

continuous precipitation technique. Sn^{2+} and Sn^{4+} show different behaviors against the precipitating and/or dissolving reagents. First, both species could form sulfide precipitates easily and they can be dissolved readily with KOH and the excess amount of $(NH_4)_2S$. However, under the excess amount of S^{2-}, Sn^{4+} is dissolved faster than Sn^{2+} kinetically. The reactions are like followings;

$$SnS(s) + 2S^{2-}(aq) \rightarrow SnS_3^{2-}(aq) \qquad \text{slow}$$

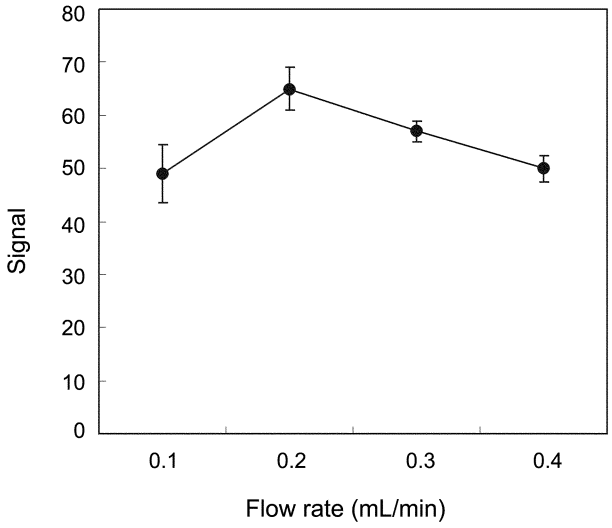

Figure 4. Signal as a function of the flow rate of thioaceteamide.

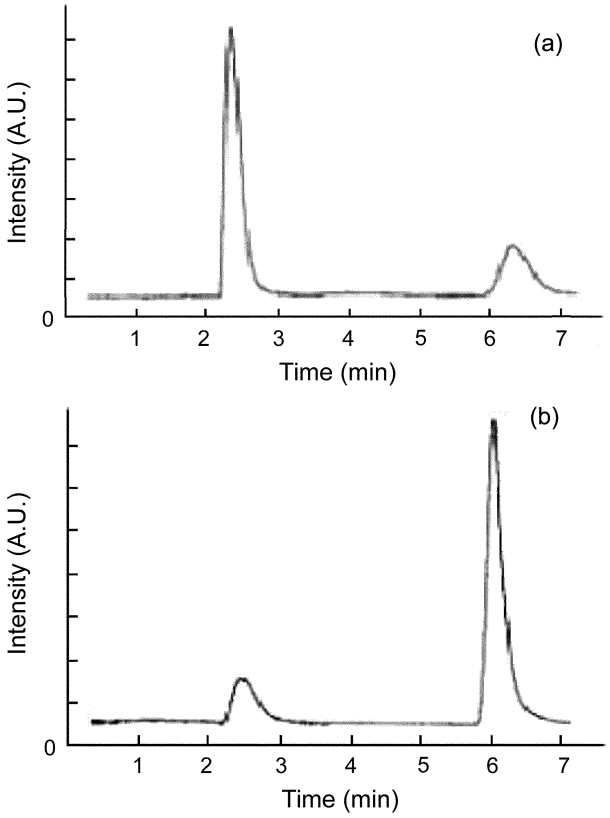

Figure 5. Different behaviors of Sn^{4+}(a) and Sn^{2+}(b) for the dissolving reagent of $(NH_4)_2S$ + HCl (adjusted at pH 7.8). The first peaks are due to $(NH_4)_2S$ + HCl and the second peaks are due to KOH. Sn^{4+} is dissolved better than Sn^{2+} to the mixed reagent but the complete separation has not been obtained.

$$SnS_2(s) + S^{2-}(aq) \rightarrow SnS_3^{2-}(aq) \qquad \text{fast}$$

By exploiting the time difference, the separation between Sn^{2+} and Sn^{4+} was considered to be possible. In a batch mode, Sn^{2+} and Sn^{4+} showed a very clear difference; *i.e.*, Sn^{4+} was dissolved completely while Sn^{2+} was not dissolving readily. However, in the continuous on-line method, the time difference between the two species was not obvious and the complete separation was not possible. Since only a very small amount of precipitates is collected unto the surface of the filter, the time difference in dissolving would not be striking as observed in a batch mode.

Secondly, it was proposed that tin sulfide precipitates show different dissolving behaviors when the dissolving reagent $(NH_4)_2S$ + HCl was employed. By the careful selection of the pH of dissolving buffer, the separation between Sn^{2+} and Sn^{4+} was successful to some degree. Equal concentration (5 ppm each) of Sn^{2+} and Sn^{4+} was mixed and examined for the separation, of which result is shown in Figure 6. Ideally, only Sn^{4+} is expected to be dissolved out by the dissolving reagent while Sn^{2+} is not. The result (Fig. 5-a) shows that Sn^{4+} precipitate was not completely dissolved and eluted out later by KOH (the second peak). Sn^{2+}(Fig. 5-b), unfortunately, was dissolved a bit by the mixed dissolving reagent of $(NH_4)_2S$ + HCl (the first peak). Most of Sn^{2+} was dissolved out by KOH (the second peak). Using the mixed dissolving reagent was successful only in part and adjusting the correct pH for the complete separation was extremely difficult.

A different precipitating reagent, instead of sulfide, could be used. Hydroxide precipitates were chosen to separate between Sn^{2+} and Sn^{4+}. NH_4OH was used as a precipitating reagent and 6 M HCl was used as a dissolving reagent. Only Sn^{2+} could form a white oxide precipitate and be collected. In Figure 6, for 10 ppm of Sn, it was shown that Sn^{2+}(a) and Sn^{4+}(b) could be separated based on the oxide precipitates formation. Sn^{2+}(a) showed a good precipitation-dissolution

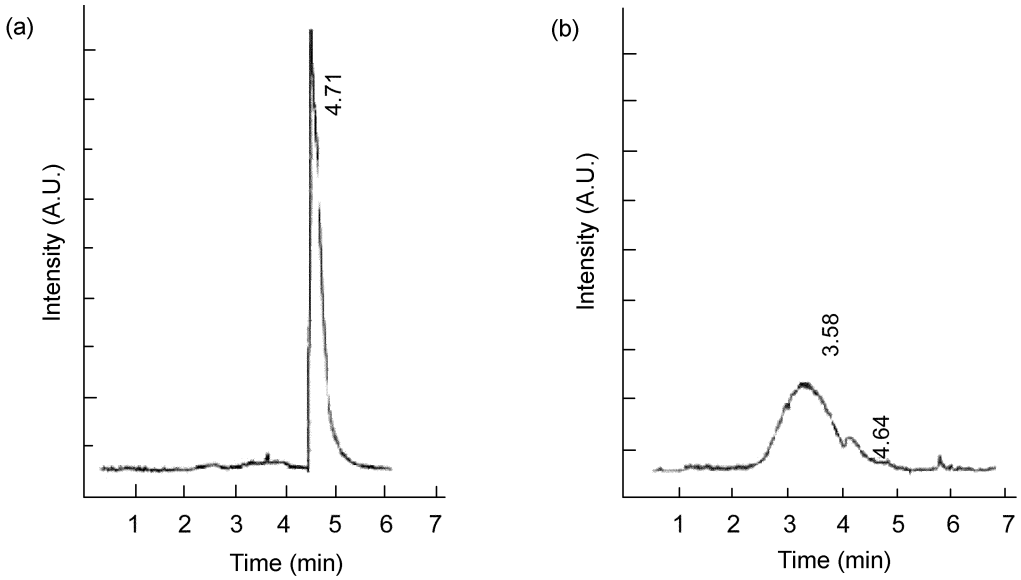

Figure 6. Separation of Sn^{2+}(a) and Sn^{4+}(b) using the oxide precipitates. Sn^{2+} is well precipitated and dissolved out by dissolving reagent, HCl, while Sn^{4+} does not form any precipitate. A broad peak at 3.58 min for Sn^{4+} represents no precipitate is formed and passes through the filter. A small change at 4.64 min (when the dissolving reagent is sent) might be suspected as an oxide precipitate.

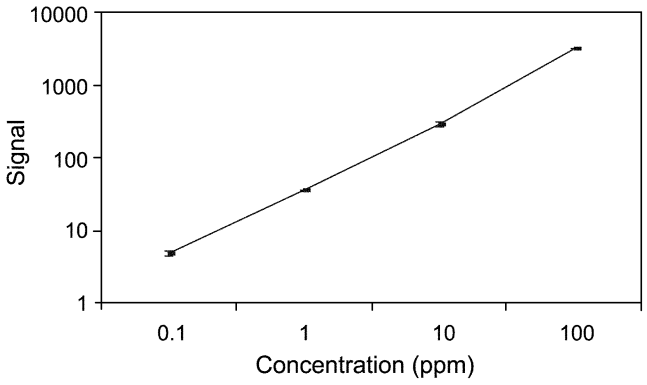

Figure 7. Calibration curve of Sn obtained with on-line sulfide precipitation system. The error bars are too small to be shown at the figure.

behavior and only a small leak was observed before the peak. Most of the sample formed precipitate well and dissolved out by the dissolving acid (HCl). Sn^{4+}(b) did not form any precipitates and no peak was observed. It could be suspected that a very small amount of precipitate might be formed as a small peak was shown when HCl was sent. It is shown that it is possible to differentiate Sn^{2+} and Sn^{4+} in continuous precipitation-dissolution method by employing proper precipitant and dissolving reagent.

Analysis of SRM (Standard Reference Material). Using the optimum condition, the accuracy of this preconcentration method was examined by analyzing tin in a NIST (National Institute of Standards and Technology) SRM 1566 (oyster tissue) sample. The solution was prepared by dissolving 0.1 gr in a concentrated nitric acid and was boiled until all organic tissue was dissolved. H_2O_2 was added further and boiled until the final volume was less than 1 mL. Finally, the sample was diluted to 100 mL. A sampling loop of 1.0 mL was used and the calibration curve was obtained for Sn and shown in Figure 7. It should be pointed out that the calibration curve was obtained with the continuous precipitation preconcentration system. The sample was analyzed and the result was 0.26 ± 0.03 ppm while the reference value was 0.25 ppm. Since the precipitation preconcentration has an advantage of the matrix separation, the result obtained from the calibration curve was appeared to be excellent.

It shows that the on-line preconcentration technique is very accurate and can be used to determine a trace concentration of elements. For a 1.0 mL of sampling, the enrichment factor calculated was 4. The enrichment factor was determined by comparing the height of the peak to the one normally obtained without precipitation. To increase the enrichment factor, a larger volume of sample could be preconcentrated. A 10 mL sampling loop, instead of 1.0 mL, was used and it was increased to 40. However, sampling speed was decreased from 15/hr to 5/hr. If speed is sacrificed, even a larger enrichment factor can be achieved.

Conclusion

In this experiment, a continuous precipitation preconcentration using the flow injection was demonstrated with the direct homogeneous sulfide precipitation of Tin group elements. Homogeneous precipitation was employed by the generation of sulfide ions from the hydrolysis reaction of thioaceteamide. The on-line direct precipitation is simple and fast yet efficient. Without adding expensive accessories, more than 40 fold enrichment can be easily achieved with the sampling speed of 5/hr. If speed is sacrificed, the concentration factor can be increased even further. Optimum conditions for homogeneous direct precipitation preconcentration were determined and used for a NIST sample. The result showed good agreement with each other. Sn^{2+} and Sn^{4+} could be separated partly with sulfide precipitate and was improved by using the hydroxide precipitant-HCl dissolving system. Though Sn was measured in this experiment, it is by no means limited to tin groups but can be expanded to many other different ions that can form precipitates.

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References

1. Valc rcel, M.; Gallego, M. *Trends in Anal. Chem.* **1989**, *8*, 34.
2. Sant'Ana, O. D.; Wagener, A. L. R.; Santelli, R. E.; Cassella, R. J.; Gallego, M.; Valcárcel, M. *Talanta* **2002**, *56*, 673.
3. González, M. M.; Gallego, M.; Valcárcel, M. *Talanta* **2001**, *55*, 135.
4. Montero, R.; Gallego, M.; Valcárcel, M. *J. Anal. At. Spectrom.* **1988**, *3*, 725.
5. Martinez-Jimenez, P.; Gallego, M.; Valcárcel, M. *Anal. Chem.* **1987**, *59*, 69.
6. Cho, Y. M.; Yeon, P.; Pak, Y. N. *Bull. Korean Chem. Soc.* **1998**, *19*, 1009.
7. Cho, Y. M.; Pak, Y. N. *Anal. Sci.* **1997**, *13*, 41.
8. Zhuang, Z.; Wang, X.; Yang, P.; Yang, C.; Huang, B. *J. Anal. At. Spectrom.* **1994**, *9*, 779.
9. Ebdon, L.; Fisher, A.; Handley, H.; Jones, P. *J. Anal. At. Spectrom.* **1993**, *8*, 979.
10. Welz, B.; Xu, S.; Sperling, M. *Appl. Spectrosc.* **1991**, *45*, 1433.
11. Park, K.; Pak, Y. N. *Bull. Korean Chem. Soc.* **1995**, *16*, 422.
12. Im, G.; Pak, Y. N. *J. of Korean Chem. Soc.* **1999**, *43*, 644.
13. Hudnik, V.; Gomiscek, S.; Gorene, B. *Anal. Chim. Acta* **1978**, *98*, 39.
14. Sherman, L. R.; Masters, J.; Peterson, R.; Levine, S. *J. Anal. Toxicol.* **1986**, *10*, 6.
15. Focus on IMO: *Antifouling Systems Moving Towards the Nontoxic Solution* (April, 1999).
16. Pablo Rodriguez-Gonzalez, P.; Encinar, J. R.; Alonso, J. I.; Sanz-Medel, A. *Analyst* **2003**, *128*, 447.
17. Monperrus, M.; Zuloaga, O.; Krupp, E.; Amouroux, D.; Wahlen, R.; Fairman, B.; Donard, O. *J. Anal. At. Spectrom.* **2003**, *18*, 247.
18. Yang, L.; Mester, Z.; Sturgeon, R. E. *J. Anal. At. Spectrom.* **2003**, *18*, 1365.