Development of Preconcentration by Continuous Sulfide Precipitation-Dissolution in ICP-AES

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The technique of on-line direct precipitation preconcentration by sulfide precipitation for As has been developed and applied to ICP-AES. For 1.0 mL of sample, the enrichment factor is 4 with the sampling speed of 15/hr. However, the enrichment factor can be increased to more than 40 times when the sampling volume is increased to 10 mL with the sampling speed of 5/hr. Analysis of NIST reference material yielded a good result with the certified value.

Keywords Preconcentration, ICP, continuous preconcentration, sulfide precipitation

Quite frequently, atomic spectroscopists have met the challenge of analysing trace levels of inorganic ions in a complex matrix. Though Inductively Coupled Plasma (ICP) has been widely used to meet the need for most samples, still it is frequently needed to preconcentrate or to separate analytes from a matrix. Precipitation has long been used in an analytical laboratory because it is a simple and fast yet efficient technique. However, the precipitation technique for preconcentration is prone to contamination from glass wares and environments in addition to from chemicals. Flow injection type of on-line precipitation is very attractive because it takes less time (20/hour) and is considerably less vulnerable to contaminations because that 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 analysed and finally, the system can be automated.

Consequently, several scientists utilized this concept and used for the analysis of Pb in a rock sample or sulfonamides based on the precipitation with Cu or Ag. This type of continuous direct precipitation has been reported earlier by Valcarcel. His group has analyzed Pb and Cu with AA utilizing on-line direct precipitation. Ammonia was used as a precipitant for Pb and organic precipitant of reubinacid for Cu. In both cases, several hundred concentrating factor was obtained.

Another type of on-line precipitation preconcentration techniques is co-precipitation which employs a collector (or carrier). Coprecipitation is also very useful in retrieving trace amounts of ions in a sample. In our group, indium was used as a collector and trace amounts of Pb and Cd was successfully analyzed in drinking water samples. However, the concentration factor was limited because of relatively large amount of precipitates collected. High back pressure at the filtering region prevented collecting large amount of precipitates. Flow rates could be slowed or stopped which results the sample throughput low.

Direct precipitation can be more advantageous in increasing concentration factor by simply collecting a large volume of sample. Since the amount of precipitate generated is less, larger quantity of sample can be preconcentrated. Direct precipitation is very simple and large amount of precipitate can be collected with a relatively high sample throughput.

Theoretically, any precipitant which has a low solubility product can be chosen to collect sample ions, whether they are cations or anions. One of the purpose of this experiment is to show that a direct precipitation technique (sulfide precipitation in this experiment) is feasible for the preconcentration. One should be able to extend to other ions easily. In this research, we report continuous direct precipitation of As with sulfide for the first time.

Experimental

In Fig. 1, a schematic diagram of the experimental system is shown. A sample is loaded with a 6-way valve. The sampling loop can be varied from 0.1 mL to several mL or more if a large concentrating factor is needed. Saturated thioacetamide to generate sulfide ion is sent to be mixed with a sample through a T-connector which is located before the reaction coil. When the valve is in "injection", sample is carried into the reaction coil after it is mixed with thioacetamide. The temperature of the reaction coil is set at 70 °C to enhance the
hydrolysis of thioaceteamide. After the reaction, precipitates are collected at the filter. After 20 seconds of washing, a dissolving reagent (KOH or ammonium sulfide) is sent for 20 seconds. Water is sent for washing and the process can be repeated for the next sample.

**Instrument**

The ICP used in this experiment is plasma 1000 of Perkin Elmer and the output is collected with an integrator (Data Jet, Spectra Physics, U. S. A.) when the peak area is to be measured. The analytical condition of ICP-AES is optimized and listed in Table 1.

A peristaltic pump from Ismatec (model Ms-CA-4) equipped with 4 channels is used. Sampling tubes used are Tygon except a Viton tube for thioaceteamide. A 6-way injection valve is made of PTFE, which is normally used in Flow Injection Analysis. For connections of tubes, 0.8 mm (i. d.) PTFE tube and barbed polypropylene fitting (Cole-Parmer Model 6365-90, U. S. A.) have been used. For reaction coil, 1.2 mm i. d. and 2.4 mm o. d. PTFE tubes are used.

**Reagents**

All water used is doubly distilled from Milli-Q water system (Millipore, Bedford, MA, U. S. A.). Standard solution of As is made from arsenic oxide. Homogeneous precipitation is used to avoid colloidal state of emulsion. Thioaceteamide is hydrolyzed at the elevated temperature and H₂S is generated *in situ*. Another advantage of using thioaceteamide is that coprecipitation is reduced by generating proper amount of sulfide ions. Excess sulfide ions adsorbed on the surface of precipitates can easily coprecipitate other cations. Saturated thioaceteamide solution is prepared by dissolving 16.3 g of thioaceteamide in 100 mL. Since pH of solution can be varied by the hydrolysis reaction, it should be fixed at 0.5 by adding HCl. Precipitates can be dissolved either by KOH or excess amount of sulfide ions.

**Results and Discussion**

**Reaction time**

The reaction time can be controlled either by varying the length of reaction coil and/or the flow rate. Precipitates are formed while the sample is mixed with thioaceteamide and passing through the heated reaction coil. The length of reaction coil should be properly chosen because a short one does not provide enough reaction time and consequently reduce the concentration factor while too long one can reduce the sample throughput. The flow rate, instead of coil length, can be changed to control the reaction time. Because of the optimum flow rate requirement of ICP, coil length is varied preferably while the flow rate is fixed at 0.95 mL/min. The length of coil is changed to 0.5 m, 2 m, and 4 m and the reaction time is calculated as 15 s, 60 s, 120 s, respectively. The relationship between the reaction time and signal is shown in Figure 2. As is expected, the signal is increasing with the length of coil because enough reaction time (between the sample and precipitant) is allowed.
Another reason might be the aging effect. When the reaction coil or the reaction time is too short, precipitates are still in a colloidal state thus easily passing through a filter. To examine the aging effect, aging time is allowed for more than 10 minutes by stopping the flow while the precipitates stay in the reaction coil. However, there haven't been any apparent changes in the signal.

Currently, reaction time of 3 - 5 minutes are provided and the coil length is limited to 3 or 4 meters long. A longer one can provide a better precision while the signal does not change much.

Temperature

Temperature is a very important parameter in producing good precipitates especially in the homogeneous precipitation using the hydrolysis of thioacetamide. A constant temperature is kept by putting the reaction coil in a temperature controlled water bath. The relationship between the temperature and signal is shown in Figure 3. In this system, the signal is not increasing much after 35 °C. However, precision becomes better at higher temperature 70 °C.

Flow Rate of Precipitant

The amount of thioacetamide could be a very important parameter in making a good precipitate. The amount of thioacetamide is varied by change of the flow rate from 0.1 mL/min to 0.4 mL/min while the flow rate of sample is fixed at 0.75 mL/min. The result is shown in Figure 4. There is no significant change with the flow rate in signal. However, in terms of reproducibility, 0.3 mL/min showed the best result. Too large flow rate can reduce the efficiency of nebulizer and signal as is shown in Figure 4.

Types of Filter

Three types of filters, paper, membrane, and stainless steel filters are used and compared with each other. A 0.45 μm stainless filter, which is used in filtering a solvent in HPLC, showed a good rigidity and could be used for a long time. Its diameter is 4 mm and thickness is 1.5 mm and the dead volume is largest among the three. Other researcher reported that the stainless filter showed good behavior but it is clogged easily and the reproducibility is the worst among the three in our experiment. A paper filter (10 μm) is very rugged and easy to handle but has shown some leaks because of the large pore size. A cellulose acetate type 0.45 μm membrane filter shows no sign of leaks but it is physically weak. After three or four runs, the precision gets deteriorated fast because it is deformed easily by the pressure applied to the filter. Table 2 shows the comparison between filters and it indicates that a membrane filter collects sample(largest signal) most efficiently. The RSD(relative standard deviation) value of membrane is better than that of a stainless filter. The best result is obtained when a membrane filter is backed with a paper filter. Even with a paper supported membrane filter, the reproducibility becomes worse after several runs. After 10 runs, filter is replaced with a new one.

Concentration of Dissolving Reagent

Ammonium sulfide and KOH dissolve As precipitates into AsS2- and AsO3+, respectively. A sharp peak is more advantageous as is in a chromatographic study. Thus, the most important factor is the ability to dissolve precipitates fast. It is observed in the experiment that both ammonium sulfide and KOH could be used well. However, ammonium sulfide can generate large

Table 2. Comparison of signals wfor different Filters

<table>
<thead>
<tr>
<th>Filter Type</th>
<th>Precipitation Efficiency</th>
<th>Reproducibility</th>
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<tbody>
<tr>
<td>Stainless(0.45 μm)</td>
<td>65.3 ± 12.5</td>
<td>62.3 ± 3.7</td>
</tr>
<tr>
<td>Paper(10 μm)</td>
<td>42.7 ± 1.8</td>
<td>62.3 ± 3.7</td>
</tr>
<tr>
<td>Membrane(0.45 μm)</td>
<td>65.3 ± 12.5</td>
<td>62.3 ± 3.7</td>
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amount of ammonia thus making the plasma unstable or even extinct. A flame could be more advantageous in this sense but the background is increasing and should be properly corrected. In ICP study, only KOH has been used. There is no significant change in signal when the concentration of KOH has been changed from 0.2 M to 4.0 M. In this experiment, 1.0 M of KOH has been used. The optimum condition of this experiment is summarized in Table 3.

Using the optimum condition, the accuracy of this preconcentration method has been examined by analysing As in a NIST SRM 1566(oyster tissue) sample. Solution is prepared by dissolving 0.1 gr in a concentrated nitric acid and is boiled until all organic tissue is dissolved. H_2O_2 is added further and boiled until the final volume is less than 1 mL. Finally, the sample is diluted to 100 mL. Sampling loop of 1.0 mL is used and the concentration is determined from the calibration curve shown in Figure 5.

The analysed value is 0.26 ± 0.03 ppm while the reference value is 0.25 ppm. It shows that on-line preconcentration technique is fast and accurate for the determination of trace concentration of elements.

For a 1.0 mL of sampling loop, the enrichment factor calculated is 4. The enrichment factor is 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 is used and the enrichment factor could be increased to 40. However, sampling speed is decreased from 15 /hr to 5/hr. If speed is sacrificed, a larger concentration factor can be achieved.

Conclusion

In this experiment, continuous precipitation preconcentration using FIA is demonstrated for direct sulfide precipitation of As. Homogeneous precipitation is employed by heating thioacetamide being mixed with sample in the reaction coil. The on-line direct precipitation is simple and fast yet efficient. Without adding expensive accessories, more than 40 fold enrichment can be easily achieved. If speed is sacrificed, the enrichment factor can be increased even more. Optimum conditions for homogeneous direct precipitation preconcentration are determined and used for the analysis of As in a NIST sample. The result shows good agreement with each other. Though As is measured in this experiment, continuous direct precipitation preconcentration can be expanded to many other different ions that can form precipitations.

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References