

Evaluation of Dissolution Methods in the Presence of High Chloride Content for the Determination of Germanium in Geological Matrices by Hydride Generation Atomic Absorption Spectrometry

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The sample dissolution is probably the most crucial step in the determination of germanium in geological and metallurgical samples due to formation of volatile germanium compounds during the course of dissolution. It has been stated that this is especially true for the samples having high sulfide and/or chloride content.¹ Several authors²⁻⁴ have reported that the use of HCl in the open vessel dissolution caused dramatic losses of germanium from various kinds of germanium containing samples. Hence HCl is replaced by an oxidizing acid, HNO₃. However, Davidson *et al.*⁵ examined the volatility losses in the course of the open vessel dissolution of a geological sample using HNO₃, HF and HClO₄ and claimed that most of the germanium (*ca.* 70%) was lost using this procedure. The initial loss was probably due to the presence of 0.06% (m/m) chloride in the sample. Shi and Jiao⁶ also mentioned a volatility loss in similar conditions. Thus closed vessel dissolution was highly recommended.

Although microwave digestion is gaining widespread use in recent years in conjunction to pressure bomb digestion methods, open vessel digestions are still very effectively used in many research or routine analysis laboratories. This study reports the statistical evaluation of the performances of open and closed vessel dissolution methods in terms of volatility losses for the determination of $\mu\text{g g}^{-1}$ concentrations of germanium in zinc plant residue samples containing very high amounts of sodium chloride (10% m/m).

Experimental

Reagents and samples

Unless otherwise stated all reagents used were of analytical reagent grade. Germanium standard solution was supplied from Aldrich Chemical Company, Inc. (Milwaukee, USA). Sodium borohydride (NaBH₄) used was a fine-granulated product (>96%, Merck). A zinc-lead smelting plant, Çinkur (Kayseri, Turkey) provided all samples analyzed in this study. They were by-products of a metallurgical recovery process of germanium from zinc plant residues and were of three compositions: i) direct leach residue samples, ii) leach residue samples mixed with

varying amounts of solid NaCl, and iii) leach residue samples mixed with varying amounts of solid NaCl and heated up to 800°C.

Apparatus

An atomic absorption spectrometer, Philips Pye Unicam PU 9200, with an N₂O-C₂H₂ flame was used. The solutions with high concentrations of germanium were aspirated directly to the flame whereas the solutions with low germanium concentrations were analyzed by utilizing a hydride generation system equipped with a liquid nitrogen trap.^{7,8}

Dissolution of samples

The wet digestion procedures used in this study were adapted from the works of Halicz¹ and Marshall⁹ with slight modifications. At the end of each dissolution, the obtained solution was diluted to 25 ml with deionized water.

Closed. To the ground sample (0.5 g) placed in the PTFE beaker of acid digestion bomb, concentrated HF (5 ml) and concentrated HNO₃ (5 ml) were added; then the bomb, after being sealed very securely, was left in an oven at 110°C for 8 h.

Open-1. To the ground sample (0.5 g) placed in a platinum crucible, concentrated H₃PO₄ (5 ml), concentrated HF (5 ml) and concentrated HNO₃ (5 ml) were added; then the crucible was heated on a hot plate until a thick syrupy residue was obtained. After the crucible was cooled down to room temperature, a second portion of concentrated HF (10 ml) was added. The solution was heated on the hot plate again until the volume was reduced to approximately 5 ml.

Open-2. To the ground sample (0.5 g) placed in a PTFE beaker, concentrated HClO₄ (10 ml) and concentrated HNO₃ (10 ml) were added; the beaker was heated gently for 2 h on a hot plate. After the beaker was cooled down to room temperature, concentrated HF (10 ml) and a second portion of concentrated HClO₄ (5 ml) were added; the mixture was reheated until the volume was reduced to approximately 10 ml.

Results and Discussion

The mentioned three samples were analyzed in eight replicates ($n = 8$). Leach residue sample itself has a natural chloride concentration of (0.04% m/m) which is far below the chloride concentrations of the other two samples. Leach residue samples which were mixed with 10% (m/m) NaCl and heated up to 800°C have noticeably lower (*ca.* 40%) germanium

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Table 1 Germanium concentrations ($\mu\text{g g}^{-1}$) in leach residue and in various samples^a

Sample	<i>n</i> ^b	<i>Closed</i>	<i>Open-1</i>	<i>Open-2</i>
LR ^c	8	46.0±4.0	40.0±3.0 ND ^d	39.0±2.0 SD ^e
LR + NaCl (10%)	8	47.2±5.0	41.7±4.2 ND	40.9±4.3ND
LR + NaCl (10%) + R ^f	8	24.3±3.2	19.2±1.4SD	18.8±2.2SD
2nd purification residue ^g	3	107±3	108±19ND	114±4ND
Old copper cake ^g	3	1116±117	1130±15ND	1094±116ND
New copper cake ^g	3	1375±42	1325±7ND	1339±49ND
1st purification residue ^g	3	1500±20	1467±65ND	1522±29ND

a. Results are given as (mean value \pm standard deviation).

b. *n*: number of dissolutions carried out.

c. Residue after H₂SO₄ leaching of zinc ore or zinc concentrate.

d. ND: statistically "not different" according to students' *t* test.

e. SD: statistically "different" according to students' *t* test.

f. R: roasted (heated up to 800°C).

g. purification precipitates obtained from leach solution before "electro gaining" of zinc metal.

concentrations compared to the other two. Hence the samples can be classified as having i) natural germanium and chloride concentration, ii) natural germanium and high chloride concentration and iii) low germanium and high chloride concentration. The results from the dissolution procedures are given in Table 1. Statistical evaluation of the data was done according to students' *t* test at a confidence level of 95%.¹⁰ Results from the case *Closed* were assumed to be accurate⁵ and the results from the cases *Open-1* and *Open-2* were evaluated. As can be seen from Table 1, open vessel dissolution procedures give lower results compared to the closed one, for the first three sets of samples. However, except the result of leach residue *Open-2 digestion*, the differences become significant when the concentration of germanium was less than 47 $\mu\text{g g}^{-1}$. These results show that the oxidizing environment in the acid mixtures might have stabilized the germanium in the solution and prevented its loss to a great extent even at very high chloride concentration. In addition, it can be said that the concentration of germanium in the sample has a more pronounced effect than that of the chloride. To clarify this fact, the efficiency of the dissolution procedures was also checked through the analysis of samples containing higher germanium concentrations. Old and new copper cakes, 1st and 2nd purification residues were obtained from the same plant. The results are also given in Table 1. As expected, the results of open vessel dissolution procedures are generally lower but

statistically not different at all than the results obtained by closed vessel dissolution procedure.

Under these circumstances, it can be concluded that there is a possibility of losing germanium in the presence of chloride when acid digestion procedures are carried out in open vessels. But the volatility loss is likely to be more pronounced if the concentration of germanium is very low. According to our observation, an approximate germanium concentration of 100 $\mu\text{g g}^{-1}$ can be considered as a critical value above which both open and closed vessel digestion methods with the recommended proportions of mineral acids can be used without any significant loss. Use of closed vessel digestion methods is recommended for the analysis of samples having lower germanium concentrations to be on the safe side.

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