

A Rapid Method for the Determination of Gallium and Germanium in Solid Samples by Atomic Absorption Spectrometry

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INTRODUCTION

Gallium and germanium are strategic elements used in such high-technology applications as computer chips and fiber optic systems. The use of these metals is expected to increase significantly during the next ten years (1,2). Unfortunately, these metals do not occur naturally as concentrated ores. In fact, only one gallium-germanium ore source, the Apex Mine near St. George, UT, has been identified and mined in the last ten years, and this material contains less than 0.1% germanium and gallium (3).

To alleviate any future domestic shortages, the U.S. Bureau of Mines, Salt Lake City Research Center (SLRC), has actively sought new gallium and germanium resources and researched ways of extracting these metals from medium to low grade ores. Essential to this work is the ability to accurately measure concentrations of gallium and germanium down to 0.01%. At SLRC, two analytical techniques, simultaneous Inductively Coupled Plasma Spectroscopy (ICP) and Neutron Activation Analysis (NAA), have been used for quantitative determination of these metals. However, significant problems have been experienced with both techniques.

A limited detection range along with common interference problems associated with high ionic

ABSTRACT

The U.S. Bureau of Mines has developed a rapid microwave digestion technique for dissolving both gallium and germanium in solid matrices that allows for accurate analysis by flame atomic absorption spectrophotometry. Microwave digestion in sealed Teflon vessels is accomplished in approximately 2 minutes/sample in a two-step process using HNO_3 , HF , H_3BO_3 , and KNO_3 . Gallium and germanium in the produced solutions are determined with no detectable interferences using nitrous oxide-acetylene flame atomic absorption spectrophotometry. With this method, samples containing as little as 0.01% gallium and germanium can be accurately analyzed. Values obtained for gallium agree with certified values and neutron activation analyses. Both gallium and germanium spike recoveries approach 100% when taken through the digestion process. The solutions produced by this method are also suitable for analysis by electrothermal atomization.

concentrations has curtailed the usefulness of ICP for gallium and germanium analyses. Of the many ores and residues analyzed, specific quantitative results were unattainable for material containing less than 0.03% gallium and germanium. With these detection limits, ICP analysis of low grade ores before or after metal extraction has been limited for scientific studies.

Interfering ions, particularly manganese and rare earths, have proven detrimental to germanium and gallium determinations using ICP. For example, ICP results indicated a major germanium find near Moab, UT. Further investigation using synthetic mixtures showed that this ore actually contained no germanium. The high manganese concentration (25%) of the sample caused an interference resulting in high germanium readings. As another example, ICP analysis of a rare earth sample (from a deposit in California) indicated that the ore contained 0.1% germanium and 0.08% gallium. Synthetic mixtures revealed that rare earth interferences had skewed the gallium and germanium results; the ore actually contained no gallium or germanium.

NAA uses a nuclear reactor to activate gallium for analysis. Germanium is not determined in our lab by NAA because of activation problems, a short half life, and manganese interference. Although SLRC has access to a nuclear reactor at the University of Utah, most analytical laboratories do not. Even with the available reactor, strict safety standards have led to an average operational down time of 50%, making this an unreliable method of analysis.

Another method used for gallium and germanium determination is atomic absorption spectrometry, both electrothermal atomization (EAAS) (4-11) and flame (FAAS) (5, 12). Each method has advantages and draw-

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backs. For example, EAAS can be used to detect gallium and germanium in the $\mu\text{g/g}$ range, but the sample preparation techniques are often labor-intensive, requiring numerous steps. In addition, EAAS is plagued by many interferences which frequently can only be eliminated using the tedious method of standard additions (11) or solvent extraction (4,9). Flame spectrometry is much faster than EAAS and is suitable for analyses down to 0.01%. However, previously developed FAAS techniques for gallium and germanium determination require lengthy digestion procedures (5) and solvent extraction methods (12).

Our laboratory developed a rapid analytical technique using a single microwave digestion to dissolve solids containing gallium and germanium. Both elements were determined from the same digestion solution using nitrous oxide-acetylene FAAS. A batch of 20 samples takes approximately one hour for complete preparation and analysis. Ores and solids containing as little as 0.01% gallium and germanium can be quickly and accurately analyzed using this technique.

EQUIPMENT AND MATERIALS

Apparatus

A Perkin-Elmer® Model 5100* atomic absorption spectrophotometer, equipped with a deuterium arc background corrector, an AS-51 autosampler, and a Perkin-Elmer 7700 computer with a PR-310 printer, was used for analysis.

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Savillex Teflon 50-mL pressure digestion vessels were used in a Sears Kenmore Model #88861 microwave oven having a maximum output of 700 watts for microwave dissolution of the samples. For safety reasons to control acid fumes, the microwave oven was modified with an exhaust duct and vented to a hood.

Reagents

All reagents were of analytical reagent grade or better. Solutions were prepared using Barnstead NANOpure II double-deionized water. Standard solutions of 10, 20, 50, and 100 mg/L Ga and 20, 50, 100, and 200 mg/L Ge were prepared in the same matrix as the samples, i.e., 5% (w/v) HNO_3 , 3% (w/v) HF, 25 g/L H_3BO_3 , and 2 g/L K. Stock solutions of HNO_3 -HF (1:1) acid mixture, saturated H_3BO_3 , and 20 g/L of K as KNO_3 were prepared for use in the microwave dissolution procedure.

Samples

The samples used in this study were a primary gallium and germanium ore from the APEX Mine near St. George, UT, and a zinc processing waste residue from Jersey Miniere Zinc (JMZ) of Clarksville, TN. The APEX material was characterized mineralogically as goethite, jarosite, and hematite, with some secondary copper minerals. The zinc residue consists of sphalerite, gypsum, quartz, and some anglesite. These samples, which contain less than 1% gallium and germanium, were prepared for further analyses by drying, grinding to -200 mesh, and thoroughly mixing.

PROCEDURE

The digestion technique developed for gallium and germanium determination uses 0.5-g samples in Savillex Teflon vessels. (A set of 12 vessels was used for the specified heating times in the micro-

wave oven.) After adding 5 mL of 1:1 HNO_3 -HF acid mixture and securing the lids with a Savillex wrench, the vessels were placed in the microwave oven and heated at 25% power for approximately 12 minutes. (Avoid heating the vessels excessively since the Teflon may fatigue and allow leakage of acid fumes to the interior of the microwave oven.) To prevent volatilization of gallium or germanium halides, the vessels were removed immediately and completely cooled in a water bath before opening and adding 25 mL saturated H_3BO_3 acid and 5-mL KNO_3 solution. With the lids securely replaced, the vessels were returned to the microwave oven and heated at full power for approximately 6 minutes. The vessels were again completely cooled in the cold water bath prior to transferring the contents to 50-mL volumetric flasks and bringing to volume with deionized water.

Following digestion, the samples were analyzed by FAAS. Table I shows the FAAS operating conditions and the working range required to determine gallium and germanium. A nitrous oxide-acetylene flame provided interference-free germanium readings. Gallium ionization was suppressed by adding KNO_3 to all solutions to give a final concentration of 2 g/L K.

RESULTS AND DISCUSSION

Sample Digestion

A principal concern when performing any digestion method for gallium and germanium is the presence and/or production of chloride ion with subsequent volatilization of GaCl_3 and GeCl_4 ; GaCl_3 volatilizes at 201°C while GeCl_4 loss occurs at 84°C (13). An open Teflon beaker digestion process using HNO_3 , HF, and HClO_4 , similar to Mintek's procedures for germanium (4) and gal-

TABLE I
Operating Conditions for Gallium and Germanium by FAAS

	Ga conditions	Ge conditions
Wavelength	287.4 nm	265.1 nm
Slit setting	0.7 nm	0.2 nm
Lamp type	Hollow cathode	Electrodeless discharge
Lamp current	10 mA	7 watts, continuous
D ₂ -background corrector	Yes	Yes
Recommended flame	N ₂ O/C ₂ H ₂	N ₂ O/C ₂ H ₂
Flame conditions	Lean, 5-10 mm cone	Rich, 20-30 mm cone
Working range	0 to 100 mg/L	0 to 200 mg/L
Detection limit	0.5 mg/L	1 mg/L
Standard matrix	5% (w/v) HNO ₃ 3% (w/v) HF 25 g/L H ₃ BO ₃ 2 g/L K	5% (w/v) HNO ₃ 3% (w/v) HF 25 g/L H ₃ BO ₃ 2 g/L K

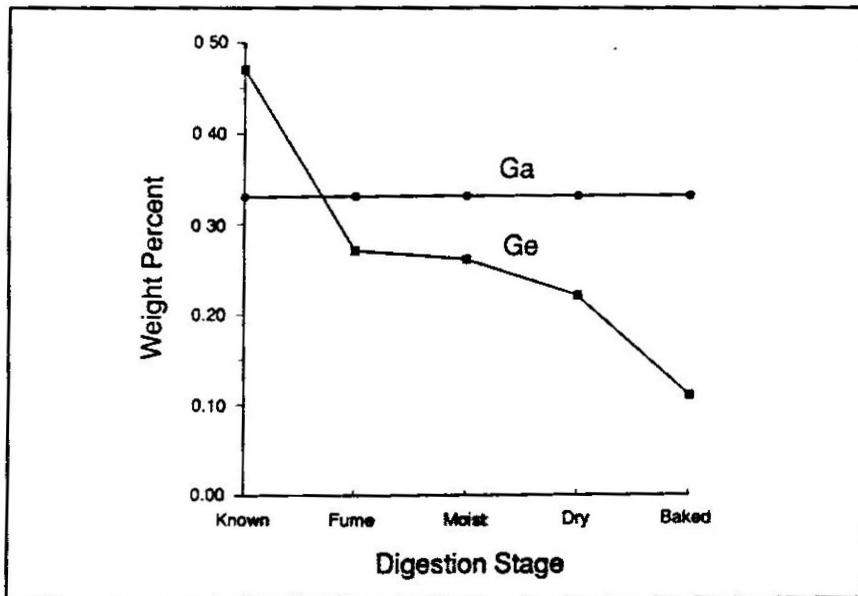


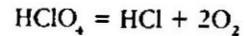
Fig. 1. Open Teflon beaker digestion of solids using HNO₃, HF, HClO₄ acids with hot plate surface temperature controlled at 200°C. Resulting solutions analyzed by FAAS.

lium (5) determination, was investigated using JMZ residue. No organic extractions were performed after sample digestion for germanium determination. The hot plate temperature was controlled at 200°C as prescribed to avoid the loss of gallium as a chloride. The solutions were analyzed

by FAAS and the results are shown in Figure 1.

The data indicate that Mintek's method was acceptable for gallium determination; however, most of the germanium was lost using this procedure. The initial germanium loss was probably due

to the presence of chloride in the sample (0.06%). The additional loss during heavy fuming of the perchloric acid to the semi-hard and baked state was likely due to chloride production. At heavy fuming, perchloric acid decomposes releasing oxygen (14) and free chloride according to the reaction (15) as follows.

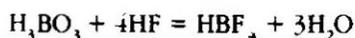


The chloride then reacts with germanium to form GeCl₄. When these reactions occur in an open beaker, the germanium is lost and cannot be recovered.

Mintek also recommended an alternate microwave digestion for germanium determination (4) using HNO₃ and HF acids; however, they were unsuccessful in applying microwave digestion to gallium determination (5). To test the applicability of microwave digestion to both gallium and germanium determination in the presence of chlorides, JMZ residue was digested using the method described under PROCEDURE, except that HCl (5 mL) was added with the initial additions of HNO₃ and HF acids. The results of this test (Figure 2) show that both gallium and germanium can be accurately recovered using microwave digestion. These results are significant as well, because they show that even if chloride is present when this procedure is used, gallium and germanium will not be lost as volatile chlorides.

Two sets of statistical tests were run to determine the significance of each of the acids, HF, HNO₃, and H₃BO₃, added in the microwave digestion procedure. The JMZ residue containing 0.33% Ga and 0.47% Ge as reported by JMZ was used for these tests and the results are given in Tables II and III.

These data show that accurate gallium and germanium determination was obtained using a combination of HF and H₃BO₃ acids. Because HF has the ability to dissolve gallium and germanium, the dissolution process without HF additions was not tested. Gallium and germanium precipitate as fluorides in weak HF acid solutions. Therefore, these tests demonstrate the effect of HNO₃ and H₃BO₃ to help dissolve precipitated fluorides. With HF alone, the determination of gallium and germanium was low. When HNO₃ was added with the HF, gallium and germanium extractions increased. However, when H₃BO₃ was added with the HF, gallium and germanium were completely extracted; the addition of H₃BO₃ in the presence of HF helps dissolve any precipitated fluorides (16), thus increasing metal extraction. In addition, H₃BO₃ complexes any free HF that is present after digestion by the following reaction:



This reaction, which neutralizes the hazards of HF, is especially important if the FAAS instrument contains glass beads in the atomization chamber.

Nitric acid addition is known to help stabilize dissolved samples; the HNO₃ assures that the gallium and germanium remain in solution. Although HNO₃ was not needed in the dissolution of JMZ residue, it is commonly used in the dissolution of many solid samples.

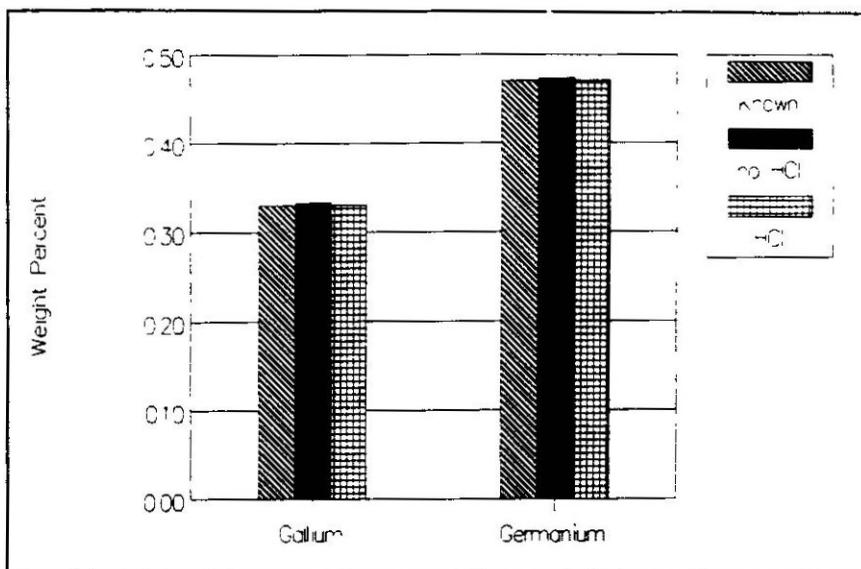


Fig. 2. Comparison of microwave digestion for gallium and germanium extraction showing the effects of hydrochloric acid addition. Resulting solutions analyzed by FAAS.

TABLE II
Microwave Digestion for Gallium Determination

HF 2.5 mL Yes/No	HNO ₃ 2.5 mL Yes/No	H ₃ BO ₃ 25 mL Yes/No	FAAS analyzed % Ga
Yes	No	No	0.24 ± 0.011
Yes	Yes	No	0.31 ± 0.001
Yes	No	Yes	0.33 ± 0.002
Yes	Yes	Yes	0.33 ± 0.004

TABLE III
Microwave Digestion for Germanium Determination

HF 2.5 mL Yes/No	HNO ₃ 2.5 mL Yes/No	H ₃ BO ₃ 25 mL Yes/No	FAAS analyzed % Ge
Yes	No	No	0.38 ± 0.014
Yes	Yes	No	0.44 ± 0.013
Yes	No	Yes	0.47 ± 0.002
Yes	Yes	Yes	0.46 ± 0.001

Sample Analysis

Certified standards (i.e., from the National Institute of Standards and Technology) or reference materials containing greater than 0.01% gallium and germanium were unavailable. However, other reliable methods were used to test the accuracy of the Bureau's procedure. These include recovery of spikes and comparison with other methods of analyses.

Recovery of Spikes

In the recovery of spikes, solutions prepared from 1000 mg/L Ga and Ge liquid standards were added to 0.5 g of JMZ residue. The solids were then taken through the Bureau's digestion sequence before analysis by FAAS. Tables IV and V show the recovery results for gallium and germanium, respectively.

As seen, the recovery of spiked gallium using the developed procedure ranged from 90% to 98%. The recovery for spiked germanium was higher, ranging from 98% to 100%. This is an indication that the method is indeed reliable.

Comparison With Other Methods

A variety of samples including JMZ residue (samples before and after leaching), Apex ore, an NBS gallium standard (<0.01% Ga), and synthetic mixtures of gallium and germanium oxides with iron and calcium oxides were analyzed for gallium and germanium using the following methods: the Bureau's FAAS procedure, EAAS, ICP, and NAA. The results are shown in Tables VI and VII.

The data show that the developed procedure provided quick and accurate analyses by FAAS. In addition, the prepared solutions yielded accurate results when EAAS was used. (A detailed description and discussion of the

TABLE IV
Gallium Recoveries From Spiked Solids

Ga added mg	Ga determined mg	Ga recovered	
		mg	%
0.00	1.75 ± 0.04	NA	NA
0.50	2.20 ± 0.01	0.45	90
1.00	2.73 ± 0.03	0.98	98
2.00	3.70 ± 0.04	1.95	97.5

NA - Not applicable

TABLE V
Germanium Recoveries From Spiked Solids

Ge added mg	Ge determined mg	Ge recovered	
		mg	%
0.00	2.40 ± 0.02	NA	NA
0.50	2.90 ± 0.02	0.50	100
1.00	3.38 ± 0.01	0.98	98
2.00	4.39 ± 0.04	1.99	99.5

NA - Not applicable.

TABLE VI
Comparison of Various Methods for Gallium Determination

Sample source	Known	FAAS	% Gallium		
			NAA	EAAS	ICP
JMZ	0.33	0.33	0.32	0.33	0.32
Apex	0.03	0.03	0.032	0.033	<0.05
NBS 1633a	0.0058	0.01	0.0059	0.006	NT
Synthetic 1	0.055	0.06	0.06	NT	<0.03
Synthetic 2	0.500	0.52	0.49	NT	0.58
Sample A	NK	0.08	0.086	0.080	<0.12
Sample B	NK	0.35	0.35	0.37	0.37

NT - Not tested.

NK - Not known.

determination of gallium and germanium by EAAS is beyond the scope of this paper and would require more expensive equipment and tedious procedures.) Finally, the test data show that samples containing minor amounts of gallium and germanium (in the range of 0.03% to 0.12%) were not accurately or dependably determined using simultaneous ICP.

CONCLUSION

The U.S. Bureau of Mines has developed a digestion technique using FAAS for determining gallium and germanium down to 0.01%. The advantages of the microwave technique over other digestion procedures are:

1. Both gallium and germanium can be accurately determined from the same digestion solution by EAAS and the more rapid FAAS.
2. No long, tedious digestion method is involved.
3. Any chloride present in the ore/residue can be tolerated.
4. No solvent extraction to remove interferences is used.

In addition, the technique has the following advantages over NAA and ICP:

1. No nuclear reactor or other equipment for storing and counting radioactive decay products is needed.
2. The FAAS method has been shown to be both accurate and rapid for the determination of gallium and germanium down to 0.01%.

Received December 1, 1989.

TABLE VII
Comparison of Various Methods for Germanium Determination

Sample source	Known	% Germanium		
		FAAS	EAAS	ICP
JMZ	0.46	0.47	0.477	0.46
Apex	0.09	0.09	0.090	0.09
Synthetic 1	0.055	0.05	NT	<0.057
Synthetic 2	0.500	0.49	NT	0.46
Sample A	NK	0.08	0.080	0.07
Sample B	NK	0.36	0.36	0.30

NT - Not tested.

NK - Not known.

REFERENCES

1. B. Petkof, *Gallium. Mineral Facts and Problems*, BuMines, 291 (1985).
2. P.A. Plunkert, *Germanium. Mineral Facts and Problems*, BuMines, 317 (1986).
3. G. Dillard, *Hazen Research Designs and Builds One-of-a-Kind Plant for Apex*, Intermountain Pay Dirt, 3A (December 1983).
4. G.D. Marshall, "The Sensitive Determination of Germanium By Atomic-Absorption Spectrophotometry Using Electrothermal Atomization," Mintek Report No. M358 (June 1988).
5. G.D. Marshall, "The Determination of Gallium in Carbonaceous Materials by Atomic Absorption Spectrophotometry," Mintek Report No. M276 (October 1986).
6. Y. Sohrin, K. Isshiki, and T. Kuwamoto, *Talanta* **34** (3), 341 (1987).
7. F. Takekawa and R. Kuroda, *Talanta* **35** (9), 737 (1988).
8. Y. Zheng and D. Zhang, *Gaodeng Xuexiao Huaxue Xuebao* **9** (2), 192 (1988).
9. M. Zheng, *Fenxi Huaxue* **15** (11), 1032 (1987).
10. S. Xian-quan, Y. Zhineng, and N. Zhemung, *Anal Chem.* **57** (4), 857 (1985).
11. D.C. Barron and B.W. Haynes, *Analyst* **111**, 19 (1986).
12. S.A. Abbasi, *Int. J. Environ. Anal. Chem.* **33** (2), 149 (1988).
13. R.C. Weast, *Handbook of Chemistry and Physics*, 55th ed., Chemical Rubber Co., 92 (1974).
14. F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th ed., John Wiley and Sons, 114 (1988).
15. B.S. Hopkins and J.C. Bailar, Jr., *Chemistry for Colleges*, 4th ed., D.C. Heath and Company, 216 (1951).
16. S.A. Matthes, R.F. Farrell, and A.J. Mackie, "A Microwave System for the Acid Dissolution of Metal and Mineral Samples," BuMines Technical Progress Report **120**, 9 (1983).

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Analysis of Metals by Graphite Furnace AAS
Using Spark Ablation

B.V. L'vov and A.V. Novichikhin.....1

A Rapid Method for the Determination of Gallium
and Germanium in Solid Samples by Atomic
Absorption Spectrometry

**Robert A. Davidson, Donna D. Harbuck,
and Dwight D. Hammargren**7

Determination of Selenium and Tellurium in Lead Alloys
by Graphite Furnace and Hydride Generation
Atomic Absorption Spectrometry

Gregory J. Fox.....13

Determination of Rare Earth Elements in Japanese Rock
Standard by Inductively Coupled Plasma-Mass Spectrometry

V. Balaram, C. Manikyamba, S.L. Ramesh, and V.K. Saxena19

Technical Note

Determination of Hydride-Forming Elements with
the FIAS-200 Flow Injection-Mercury/Hydride System

T. Guo, W. Erler, H. Schulze, and S. McIntosh24

Bibliography

Atomic Spectroscopy Bibliography July-December 1989

Anneliese Lust.....29

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