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RECENT ANALYTICAL METHODS FOR THE ELEMENT GERMANIUM IN GEOCHEMICAL SAMPLES

by

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UNITS AND ABBREVIATIONS

The metric system of units is used in this report. The abbreviations for units are as follows:

% (percent)
ppm (parts per million)
ppb (parts per billion)
ug/l (micrograms per liter)
mg (milligrams)
^{o}C (degrees Celsius)
um (micrometers)

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ABSTRACT

Methods for the determination of the element germanium in geological materials, appearing in the geochemical literature during the last decade, have been reviewed and compiled. Methods are grouped into the analytical disciplines of optical spectroscopy (emission and absorption), x-ray spectrometry, mass spectrometry, activation analysis and "wet" chemical analysis. Works consisting of compiled standard reference sample data with the inclusion of Ge are also listed; and items for consideration, when choosing a method of analysis for Ge, are discussed.

INTRODUCTION

The occurrences and practical, economic, and geochemical aspects of germanium have been enumerated by Weber (120), Bernstein (110), and Ingamells (48).

Germanium concentrations on the order of 4 ppm and less in most rocks and ores while those in metamorphic rocks are usually less than 8 ppm (39, 44 and 110). Levels as high as 3000 to 7000 ppm in sphalerite, geothite and hematite deposits have been observed (110). Germanite and argyrodite, which contain 5 to 7% Ge, are examples of few naturally-occurring germanium-bearing minerals. Ge levels up to 100 to 200 ppm are found in low grade coals (48), and 0.3 to 1.4% Ge has been found in coal from northeast India (102). The natural abundance of Ge in seawater is 0.5 to 0.6 ppm (39 and 44), and in meteorites Ge levels from less than 1 ppm to over several thousand ppm have been determined (110).

During the last decade, various analytical methods for germanium in geological materials have been described in more than 120 journal articles. Analyzed materials include minerals and rocks; ores and mining-process products; meteorites and other astrogeological specimens; lignite, coal and coal waste products; fresh, marine, and geothermal waters; and river and marine sediments.

The dominant instrumental method is optical spectroscopy which includes the emission methods of d. c. arc spectroscopy (1-3, 5-6, 8-17, 20-22, 24, 26-30, 32-34, 109 and 112), plasma emission spectrometry (19, 25 and 31), atomic fluoresence spectroscopy (23), and laser induced spectroscopy (7). Optical methods based on absorption include flame and flameless atomic absorption spectrophotometry, often in conjunction with hydride generation (35-36, 40-43, 45-46, 53, 125, 134 and 137), and uv-vis spectrophotometry (37-38, 47-49, 51-52, 54, 56-58, 112, 117, 124, 129-131, 133 and 135) where phenylfluorone, which is specific for germanium, is commonly used.

X-ray spectrometry, mainly involving both x-ray fluorescence (XRF) and particle-induced x-ray emission (PIXE), is the next most reported method (59-74), followed by mass spectrometry (spark-source, secondary-ion and laser-source) (61 and 75-85) and by neutron activation analysis (61, 86-87, 91-94 and 96-99) and other activation methods (88-90 and 95).

Aside from sample preparation by decomposition and separation in the chemical laboratory before final measurement by the above methods, detection by "wet" methods still prevail. Some consider uv-vis spectrophotometry, mentioned above, in this category of methods. Gravimetric (48 and 102) and titrimetric procedures (104 and 106) as well as separations by paper chromatography (103) and high-performance liquid chromatography (100) have been reported. Applications of polarography (101, 105, 107-108, 128 and 136) exist.

In addition to comprehensive compilations of Ge values in silicate reference samples (123 and 125), compilations of recently-released reference samples containing Ge data (109, 111 and 121) have appeared in Chemical

Abstracts. Works appearing in Chemical Abstracts without mention of methods (111-116, 118 and 121-122) are concerned primarily with elemental abundances in the samples under study.

OPTICAL SPECTROSCOPY

D. C. arc methods used at the U. S. Geological Survey are based on the work of Bastron and others (4) and Myers and others (18) and are considered rapid techniques having RSD's on the order of 5 to 18% (6 and 24). Different matrices are compensated for with the use of spectral buffers (3, 8, 12, 16, 28 and 33) and detection limits of 0.1 to 10 ppm can be expected (4, 6, 8, 18 and 30). Sample preparation include fusion followed by solvent extraction (5), preconcentration on other solids (13 and 20) and chemical treatment in arc electrodes (14).

Inductively-coupled plasma-atomic emission spectrometry (ICP-AES) has been applied to coal ash, with precision and accuracy of 10% or better and a detection limit of 0.1 ppm (19), and to geological materials (25). A high-frequency ICP source with performance data on Ge analysis has been reported (31). Laser-induced emission spectroscopy (7) has been used to determine Ge in sulfide minerals.

Direct analysis by atomic absorption spectrometry (AAS) include flame analysis of lignite ash with a detection limit of 0.01 ppm (41) and graphite furnace analysis of coal (127), iron-rich natural waters (43) and sediment solids with a detection limit of 0.03 ppm (40). Low results can arise with direct use of the graphite furnace due to volatilization of Ge from the graphite tube prior to atomization (48 and 126).

Hydride generation combined with flame and graphite furnace AAS has been applied to natural waters and seawater (35-36 and 46); silicates, sulfide ores, sulfide concentrates (45 and 53); and coal ash (42) in order to circumvent difficulties with direct analysis. The hydride technique affords sensitivities on the order of 0.03 ppm with the flame (42) and detection limits of about 0.01 to 0.02 ppm with the graphite furnace which allows for the study of germanium speciation in natural waters (46).

Reports of colorimetric methods for Ge in coal (54 and 117), lignite ash (37), coal fly ash (57), minerals (47), and other geologic materials (48 and 54) are based on the well-known specificity of phenylfluorone for Ge (44, 50 and 55). The precision of the phenylfluorone method is 4% at the 2-ppm level (39) with an error of 10% at the 1-ppm level (44). The method can be rapid and simple for sulfides and coals with a detection limit as low as 0.25 ppm (54). Other reagents for spectrophotometric analysis are known (51-52, 124, 131, and 133). Still other analytical works (38, 49, 58 and 112) have no mention of reagents in Chemical Abstracts.

X-RAY SPECTROMETRY

The potential convenience of non-destructive analysis of solids is available with energy-dispersive XRF spectrometry. However, analytical sensitivity for Ge by XRF is inadequate for most geological materials and matrix conditions. For example, the presence of cobalt can raise the detection limit of Ge from 1 to 50 ppm even with specimen preparation (73).

When low levels of Ge are determined by XRF in the presence of large concentrations of lead, Pb L-beta line corrections should be made (71).

Specimen preparation involves the pressing of pellets for coal fly ash and other geological materials (64-65), precipitation of Ge from natural waters (69-70) and precipitation from acid digests of rocks and soils (63 and 74). No sample preparation is needed for PIXE analysis of coal fly ash (59 and 68), coal macerals (72), and bituminous coal (62).

Other XRF Ge data have been presented for low rank coals (60), coal waste materials (66) and geothermal waters (61).

The use of a synchrotron radiation source for x-ray spectrometric analysis has been discussed (67).

MASS SPECTROMETRY

Spark source mass spectrometry (SSMS) has been used on meteorites (79-80), geothermal waters (85), airborne dusts and river sediments (81), chromites (75), fluorite (78) and other geological materials (76-77 and 82). Detection limits range from 0.001 to 0.1 ppm with a precision of 3 to 5% (79). Determinations on reference materials have shown agreement with published data in the concentration range of 0.1-2 ppm (80).

Secondary-ion mass spectrometry (SIMS) has been applied to analysis of small areas (8 um diameter) of geological materials (83).

ACTIVATION ANALYSIS

Neutron activation analysis (NAA) for Ge requires chemical separation after irradiation (86, 93-94 and 98-99) and prior to measurement. Detection limits are on the order of 0.01 ppm (86) with a precision of less than 10% (86 and 98). Sample irradiation for activation analysis has also been accomplished with transuranium sources (88), high-energy photons (89) and high-energy protons (90). Also radiometric methods relying on the detection of x-rays (95) and natural radioactivity (132) have been reported.

WET CHEMICAL METHODS

Aside from the already-mentioned uv-vis spectrophotometric methods, polarographic methods with detection limits as low as 0.4 ppb (ug/l) in Ge ore solutions (108) and 0.1 ppb (ug/l) in water (136) have been published. Other investigations of polarographic methods report a working range of 0.005 to 0.8 ppm Ge with ores (105 and 128) and a sensitivity of 5 ppb (ug/l) for mineral solutions (107). Minor-to-major concentrations of Ge can be determined by titrimetry (104 and 106) or by gravimetry (48 and 102). High-performance liquid chromatography (HPLC) has been applied to water analysis in order to separate the molybdoheteropoly acids of Ge, P, As and Si (100); and paper chromatography has also been used for isolation of Ge (103). The application of heteropoly compounds to germanium analysis has been reviewed (119).

REFERENCE SAMPLES AND MISCELLANEOUS STUDIES

The works of Abbey (123) and Govindaraju (125) list germanium levels in silicate reference samples from 0.88 to 25 ppm. Additional reference standard reports for Ge were for iron-formation standards (109), granite and feldspar standards (111) and drainage sediment samples (121).

Numerous studies appearing in Chemical Abstracts do not particularly mention the method used for Ge; but they include analyses of copper concentrates (116), coal and fossil fuels (113-115), saturated sodium chloride solutions (118) and sulfides (122).

MOST PRACTICAL METHOD OF ANALYSIS

The choice of method for determining gemanium should be based on physical state and size of the sample and speed, precision, detection limit and cost of analysis. If the Ge data need not be precise, then direct emission spectroscopic methods are the methods of choice with minimal sample preparation and detection limits on the order of 0.1 to several ppm on sample sizes less than 100 mg.

The most sensitive technique among the optical spectroscopic methods is hydride generation/GFAAS with detection limits and sensitivities less than 0.1 ppm, but any solid sample must be decomposed and dissolved. The graphite furnace technique suffers from memory effects (48), and inconsistent results arise from formation of volatile Ge monoxide prior to atomization (48 and 126). Because of Ge volatility in the presence of sulfur, halogens or organic matter, any ashing step should be done at a temperature of less than 400°C. Also, germanium loss can be expected with any decomposition using a flux (48).

The colorimetric phenylfluorone method, often involving distillation of $GeCl_4$, is prone to error with the presence of oxidizing agents, the slow formation and possible instability of the colored species, and the poor quality of commercially-available reagent(48). Despite these drawbacks, the method is still used and can be made simple and rapid (54).

Good precision is possible at low Ge levels with SSMS and NAA methods, but NAA methods are time-consuming and require chemical separations of hazardous radioactive specimens after irradiation. SSMS appears to be an expensive and infrequently-used method.

Non-destructive analysis by energy-dispersive XRF spectrometry is possible when lowest detection limits are not required, but levels of Ge in most rocks are below 10 ppm. PIXE spectrometry has been applied only to coal and coal byproducts.

With XRF sensitivity is improved and detection limits are lowered somewhat when sample briquets are prepared and analyzed. Chemical separation and preconcentration of Ge are necessary to eliminate matrix effects and spectral interferences encountered in XRF as well as to achieve detection limits and sensitivities comparable to the other methods already mentioned. However, chemical pretreatment of samples for XRF spectrometry, or for any other method, is time-consuming and frequent preparations of reference standards are necessary to verify the accuracy of the procedure.

If emission spectroscopy is not to be used for analysis, then important factors to consider in choosing most other methods are sample decomposition and separation of Ge from other elements interfering with its detection. The volatility of Ge compounds formed during decomposition is problematic and is suspected to be a reason for low Ge data reported in the literature (48).

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REFERENCES

The references cited in the text are taken from a computer data base and are presented in the following pages. Each citation can have up to 10 lines of information. The first line has the reference number cited in the text of this report along with the name(s) of the author(s). The second line gives the year of publication. The last line gives the volume number and identification number of the abstract appearing in Chemical Abstracts (CA) (a dash signifies that no Chemical Abstract reference information is in the data base). The data appearing from the third line to the next to the last line are the title of the paper or book, the title of the journal or publication in which the paper appears, the volume number and the pages of the journal, and any other publication information.

1. Arnautov, N. V.
1978
Direct methods for quantitative spectroscopic analysis in geochemistry
Fiz. Metody Analiza v Geokhimii, Novosibirsk
103-11
CA: 92: 225959u

2. Arnautov, N. V., Kireev, A. D., and Yakovleva, N. A.
1984
Determination of minor and dispersed elements in rocks using the MFS-4 quantometer
Metody Spektr. Anal. Miner. Syr'ya [Mater. Vses. Konf. Nov. Metodam Spektr. Anal. Ikh. Primen.] 2nd 1981
37-40
CA: 102: 71907m

3. Balakishieva, B. A.
1976
Method of quantitative spectrographic analysis of mercury, thallium, arsenic, nickel, cobalt, vanadium, and other elements in different types of rocks, Izv. Akad. Nauk Az. SSR, Ser. Nauk Zemle
(1)
108-15
CA: 86: 100439u

4. Bastron, H., Barnett, P. R., and Murata, K. J.
1960
Method for the spectrochemical analysis of rocks, minerals, ores, and other materials by a powder d-c arc technique
U. S. Geol. Survey Bull.
1084-G
165-82
CA: -

5. Doerffel, K. and Tagle, A.
1978
Spectrometric analysis of solutions of metallic ore by the stabilized arc
Z. Angew. Geol.
24(1)
51-2
CA: 89: 99096h

6. Egranova, I. G., Vall, G. A., Aolovei, N. N.
1981
Spectral determination of trace elements in rocks and minerals
Zh. Anal. Khim.
36(7)
1259-66
CA: 95: 196741w

7. Geidman, B. M. and Stoicheva, S. B.
1983
Quantitative determination of trace elements of sulfide minerals by using the LMA-1 laser microspectal analyzer
Geol. i Rudonosn. Yuga Ukrainy Dnepropetrovsk
93-6
from Ref. Zh., Geol. 1984
Abstr. No. 8V579
CA: 101: 203479q

8. Gogala, A.
1985
Some experiences with the d. c. arc excitation of geological materials
ATOMKI Kozl.
27(3)
393-7
CA: 103: 205050h

9. Gorkun, V. N.
1975
Procedure for quantitative spectral analysis of dry residues of natural waters for 23 chemical elements
Tr.-Akad. Nauk SSSR, Dal'nevost. Nauchn. Tsentr, Sakhalin, Kompleksn. Nauchno-Issled. Inst., 35
120-8
CA: 89: 30479t

10. Horvath, M.
1977
Determination of trace elements in mining products by spectrography
Banyasz. Kohasz. Lapok, Banyasz
110 (Kulonszam 2)
K139-K142
CA: 89: 139795

11. Jarkovsky, J., Plsko, E., and Stresko, V.
1978
Quantitative spectrochemical determination of microelements in chalcopyrites
Sb. Geol. Ved, Technol., Geochem.
15
59-70
CA: 90: 132302t

12. Jiang, S.
1982
Spectrographic detrmination of gallium, thallium, indium, and gallium in minerals
Fenxi Huaxue
10(2)
102-4
CA: 98: 82928u

13. Koval'chuk, L. I., Kuryukova, V. P., Smirnova, L. V., and Shabonov, E. V.
1979
Chemical-spectral determination of trace elements in sea water using preconcentration on metatitanic acid
Zh. Anal. Khim.
34(6)
1136-9
CA: 91: 162820y

14. Loginova, L. G., Arapova, R. M., and Slobodchikova, R. I.
1981
Methods for the optimization of conditions for group quantitative spectral determination of trace impurities in mineral raw material
Metod. Aspekty Izuch. Redkomet. Mestorozhd.
172-87
edited by Ovchinnikov, L. N.,
Izh. Nauka: Moscow, USSR
CA: 95: 231385g

15. Lubchenko, I. Yu., Il'icheva, L. V., Gusareva, A. I., and Turochkina, N. M.
1979
Effect of bulk composition on the quantitative spectral determination of microcomponents in the analysis of sedimentary rocks and ores
Litol. Polez n Iskop.
2
163-9
CA: 91: 82488f

16. Morozova, L. F. and Morozov, A. G.
1976
Semiquantitative analysis of mineral raw material on the DFS-8-2 spectrograph
Zavod. Lab.
42(8)
940-1
CA: 86: 83164f

17. Myers, A. T., Connor, J. J., Conklin, N. M., and Rose, H. J. Jr.
1976
Glass reference standards for trace element analysis of geological materials--compilation of interlaboratory data
U. S. Geol. Survey Prof. Paper
1013
CA: -

18. Myers, A. T., Havens, R. G., and Dunton, P. J.
1960
A spectrochemical method for the semiquantitative analysis of rocks, minerals, and ores
U. S. Geol. Survey Bull.
1084-I
207-229
CA: -

19. Nadkarni, R. A. and Botto, R. I.
1984
Determination of germanium in coal ashes by inductively-coupled plasma atomic emission spectroscopy
Appl. Spectrosc.
38(4)
595-8
CA: -

20. Oshchepkova, A. P., Raitses, V. F., and Denisova, N. A.
1977
Chemical-spectral determination of a group of volatile trace elements in mine water
Nauchno Tr.-Vses. Nauchno-Issled. Proektno-Konstr. Instr. Okhr. Okruzhayushchei Prir. Sredy Ugol'n. Prom-sti, 23
53-8
CA: 91: 145798e

21. Rait, N.
1981
Multiple-element semiquantitative analysis of one-milligram geochemical samples by d. c. arc emission spectrography
Chem. Geol.
32(3-4)
317-33
CA: -

22. Rasmy, M.
1984
Sensitive geochemical technique for the quantitative determination of trace elements in zinc sulfide ores
J. Univ. Kuwait, Sci.
11(1)
113-9
CA: 102: 124776b

23. Rigin, V. I.
1985
Multielement methods of atomic fluoresence analysis of enviromental samples
Zh. Anal. Khim.
40(4)
630-7
CA: 103: 47473s

24. Romanova, L. V. and Safronova, A. A.
1979
Spectrographic determination of gallium and germanium in phosphorites
Khim. Prom-st., Ser.: Prom-st. Gornokhim. Syr'ya
(4)
22-3
CA: 92: 51397s

25. Samuel, J., Rouault, R., and Besnus, Y.
1985
Standardized multielement analysis of geologlical materials with inductively-coupled plasma emission spectrometry
Analusis
13(7)
312-7
CA: 103: 188732n

26. Schroen, W., Kaiser, G., and Bombach, G.
1983
Emission spectrographic analysis of trace elements in geologic samples with semiautomatic plate evaluation
Z. Angew. Geol.
29(11)
559-65
CA: 100: 29038n

27. Segal, I. D. and Berenshtein, L. E.
1982
Use of experimental design for determining chalcophile elements in geological samples
Zavod. Lab.
48(7)
71-2
CA: 97: 174056r

28. Suknev, V. S. and Sukneva, L. S.
1984
Use of a refractory buffer in the simultaneous spectral determination of boron and elements with a low boiling point in geological samples
Metody Spektr. Anal. Miner. Syr'ya [Mater. Vses. Konf. Nov. Metodam Spektr. Anal. Ikh. Primen.] 2nd 1981
44-7
CA: 102: 71909p

29. Volke, P.
1978
A method for the semiquantitative general spectrographic analysis of silicate materials
Z. Angew. Geol.
24(1)
49-51
CA: 89: 84233b

30. Wu, J., Wen, Z., and Zhang, M.
1983
Emission spectrometric determination of trace arsenic, antimony, bismuth, cadmium, germanium, indium, and thallium in geological materials
Yankuang Ceshi
2(2)
133-5
CA: 100: 61054a

31. Xia, Y. and Ji, Z.
1984
High-frequency ICP-D-type plasma source
Guangpuxue Yu Guangpu Fenxi
4(6)
28-34, 44
CA: 103: 152743c

32. Yang, S.
1982
The quantitative emission spectrographic method for direct determination of gallium, indium, germanium, copper, vanadium and nickel in coals and kerogen
Diqui Huaxue, (2)
213-6
CA: 97: 58191q

33. Yankovskaya, T. A.
1974
Method for spectral analysis of microsamples of mineral powders for impurity elements from the surface of electrodes
Metody Geokhim. Anal. Gorn. Porod Prir. Vod
1974
80-103
ed. by Kuznetsov, V. A.
Akad. Bauk B. SSR: Minsk,USSR
CA: 86: 37146d

34. Yun, J. I., Yun, Y. C., and Kim, G. N.
1982
Spectrographic determination of impurities in sintered zinc ore
Punsok Hwahak
(1)
10-17
CA: 97: 103458n

35. Andreae, M. O.
1983
The determination of the chemical species of some of the "hydride elements" (arsenic, antimony, tin, and germanium) in seawater: methodology and results, NATO Conf. Ser., [Ser.] 4
9 (Trace Met. Sea Water)
1-19
CA: 98: 204079r

36. Andreae, M. O. and Froelich, P. N., Jr.
1981
Determination of germanium in natural waters by graphite furnace atomic absorption spectrometry with hydride generation
Anal. Chem.
53(2)
287-91
CA: -

37. Aznarez, J., Moneo, P., and Vidad, J. C.
1985
Extraction-spectrophotometric determination of germanium with phenyl-fluorone in N,N-dimethylforamide
Analyst
110(6)
747-9
CA: -

38. Berkovitz, L. A. and Lukashin, V. N.
1984
Three marine sediment reference samples: SDO-1, SDO-2 and SDO-3
Geostand. Newsl.
8(1)
51-56
CA: 101: 162753d

39. Burton, J. D., Culkin, F., and Riley, J. P.
1959
The abundances of gallium and germanium in terrestrial materials
Geochim. Cosmochim. Acta
16
151-80
CA: -

40. Carnick, G. R. and Barnett, W. B.
1984
Determination of germanium by Zeeman atomic absorption spectro-photometry
At. Spectrosc.
5(5)
213-4
CA: -

41. Castillo, J. R., Lanaja, J., Belarra, M. A., and Aznarez, J.
1981
Flame atomic absorption determination of germanium in lignite ash with extraction of tetrachlorogermane into hexane
Anal. Chim. Acta
2(5)
159-60
CA: -

42. Castillo, J. R., Lanaja, L., and Aznarez, J.
1982
Determination of germanium in coal ashes by hydride generation and flame atomic-absorption spectrophotometry
Analyst
107
89-95
CA: 97: 8885r

43. Criand, A. and Fouillac, C.
1985
Use of the L'vov platform and molybdenum coating for the determination of volatile elements in thermomineral waters by atomic absorption spectrometry, Anal. Chim. Acta
167
257-67
CA: -

44. El Wardani, S. A.
1958
Marine geochemistry of germanium and the origin of Pacific pelagic clay minerals
Geochim. Cosmochim. Acta
15
237-54
CA: -

45. Halicz, L.
1985
Determination of germanium in silicate rocks and sulfide ores by hydride generation and flame atomic-absorption spectrophotometry
Analyst
110(8)
943-6
CA: 104: 28023z

46. Hambrick, G. A. III, Froelich, P. N. Jr., Andreae, M. O., and Lewis, B. L.
1984
Determination of methylgermanium species in natural waters by graphite furnace atomic absorption spectrometry with hydride generation
Anal. Chem.
56(3)
421-4
CA: -

47. Hsieh, H., Cheng, Y., and Cheng, C.
1979
Extraction, separation and subsequent determination of micro-amount of germanium selenium and tellurium
Fen Hsi Hua Hsueh
7(6)
485
CA: 94: 57429s

48. Ingamells, C. O. and Pitard, F. F.
1986
Applied geochemical analysis
733 pp.
John Wiley and Sons
New York
CA: -

49. Lebedeva, L.I., Tsyganova, Z. F., and Chernyshova, E. V.
1982
Determination of germanium in quartz glass
Vestn. Leningr. Univ., Fiz. Khim.
22(4)
115-8
CA: 98: 112365c

50. Luke, C. L. and Campbell, M. E.
1956
Photometric determination of germanium with phenylfluorone
Anal. Chem.
28(8)
1273-6
CA: -

51. Mirzoyan, F. V., Tarayan, V. M., and Airiyan, E. Kh.
1985
Study and use of the reaction between malachite green and 11-molybdo-germanic heteropoly acid
Zh. Anal. Khim.
39(11)
2010-4
CA: 102: 214260h

52. Nazarenko, A.
1985
Determination of titanium(IV) and germanium(IV) with disulfophenyl-fluorone and complex cationic surfactants
Zh. Anal. Khim.
40(5)
828-33
CA: 103: 134079m

53. Robert, R. V. D.
1976
Atomic absorption determination in metal sulfide concentrates, of the elements that form gaseous hydrides
Natl. Inst. Metall., Repub. So. Africa, Rep.
1838
33pp.
CA: 86: 83231a

54. Sager, M.
1984
Bestimmung von Germanium in Gesteinen und Erzen durch Destillation und Spektralphotometrie
Mikrochim. Acta
1984 II
381-8
CA: -

55. Sandell, E. B.
1959
Colorimetric determination of traces of metals
1032 pp.
Interscience Publishers, Inc.
New York
CA: -

56. Shelton, B. J., Komarkova, E., Josephson, M., Cook, E. C. T., and Dixon, K.
1977
The determination of some trace elements in sulfides by spectrophotometry
Natl. Inst. Metall., Repub. So. Africa, Rep.
1857
31pp.
CA: 87: 47706w

57. Shida, J., Takahashi,, Y., Ojima, K., and Matsuo, T.
1984
Flotation-spectrophotometric determination of germanium with phenylfluorone in coal fly ash
Bunseki Kagaku
33(5)
E143-E149
CA: 101: 59639x

58. Zhang, J. and Chen, J.
1985
Chemical analysis of blende
Yanshi Kuangwu Ji Ceshi
4(2)
155-9
CA: 103: 188723k

59. Bacci, P., Caruso, E., Braga Marcazzan, G. M., Redaelli, P., Sabbioni, C., and Ventura, A., 1984
PIXE as a tool for elemental and size analysis of power station particulate emissions
Nucl. Instrum. Methods Phys. Res.
Sect. B 231(1-3)
522-5
CA: 101: 78332h

60. Benson, S. A.
1980
Analysis of low rank coals by x-ray fluorescence
Proc. N. D. Acad. Sci.
34
10
CA: 93: 188864g

61. Blommaert, W., Vandelanoote, R., Van't Dack, L., Gijbels, R., and Van Grieken, R., 1980
Relative evaluation of neutron activation, x-ray fluorescence, and spark source mass spectrometry for multielement analysis of geothermal waters
J. Radioanal. Chem.
57(2)
383-400
CA: 93: 79673y

62. Chen, J. R., Kneis, H., Martin, B., Nobiling, R., Traxel, K., and 1981
Chao, E. C., Trace elemental analysis of bituminous coals using the Heidelberg proton microprobe
Nucl. Instrum. Methods
181(1-3)
151-7
CA: 95: 9638b

63. Connor, J. J., McNeal, J. M., and Crock, J. G.
1979
Geochemical analysis of copper-silver-bearing rocks in the Spokane Formation (Belt Supergroup), Lewis and Clark County, Montana
U. S. Geol. Survey Open-File Rept.
79-1440
27 pages
U. S. Geol. Survey
Denver, CO
CA: 93: 197046u

64. Giauque, R. D., Garett, R. B., and Goda, L. Y.
1977
Determination of forty elements in geochemical samples and coal fly ash by x-ray fluorescence spectrometry
Anal. Chem.
49(7)
1012-7
CA: 86: 199356z

65. Giauque, R. D., Garrett, R. B., and Goda, L. Y.
1977
Energy-disperesive x-ray fluorescence spectrometry for determination of twenty-six trace and two major elements in geochemical specimens
Anal. Chem.
49(1)
62-7
CA: 86: 50275q

66. Heaton, M. G., Buyer, J. S., Hershey, J. P., Duedall, I. W., and Giauque, R. D., 1982
Elemental analysis of raw and stabilized coal waste materials
Environ. Technol. Lett.
3(12)
529-40
CA: -

67. Jaklevic, J. M., Giauque, R. D., and Thompson, A. C.
1985
Quantitative x-ray fluorescence analysis using monochromatic synchrotron radiation
Nucl. Instr. Methods Phys. Res., Sect. B
B10-11(1)
303-8
CA: 103: 188632e

68. Kraner, H. W., Hansen,, A. L., Jones, K. W., Oakley, S. A., Duedall., I. W., and Woodhead, P. M. J., 1982
Application of PIXE, RBS, and high-energy proton microbeams to the elemental analysis of coal and coal waste
At. Nucl. Methods Fossil Energy Res. [Proc. Am. Nucl. Soc. Conf.]
1980
189-204
CA: 97: 137833w

69. Marijanovic, P., Makjanic, J., and Valkovic, V.
1984
Trace element analysis of waters by x-ray emission spectroscopy
J. Radioanal. Nucl. Chem.
81(2)
353-7
CA: 100: 144710n

70. Marijanovic, P., Makjanic, J., and Valkovic, V.
1983
Trace element analysis of waters by x-ray emission
Journ. Etud. Pollut. Mar. Mediterr.
6th 1982
345-7
CA: 101: 157347v

71. Marinenko, R. B.
1984
Use and abuse of quantitative wavelength-dispersive x-ray microanalysis
Microbeam Anal.
19th
201-4
CA: 101: 143071p

72. Minkin, J. A., Chao, E. C. T., Thompson, C. L., Nobiling, R., and Blank, H.
1982
Proton microprobe determination of elemental concentrations in coal macerals
Scanning Electron Microsc.
(1)
175-84
CA: 98: 128892h

73. Verbeke, P. and Adams, F.
1979
Multi-element analysis of geological substances by energy-dispersive x-ray fluorescence
Anal. Chim. Acta
109(1)
85-95
CA: -

74. Wahlberg, J. S.
1975
Analysis of rocks and soils by x-ray fluorescence
in U. S. Geol. Survey Open-File Rept.
75-436
69-70
U. S. Geol. Survey
Denver, CO
CA: -

75. Agiorgitis, G., Panagos, A., and Marien, R.
1976
Determination of rare elements in Greek chromites
Chem. Erde
35(2)
199-201
CA: 86: 64997p

76. Bulaceanu, R. and Dumitrescu, P.
1976
Spark source mass spectrometry for trace analysis in geological samples
Rev. Chim. (Bucharest)
27(10)
894-6
CA: 86: 164755b

77. Dietze, H. J.
1981
Mass spectrometric analysis of standard rocks
ZfI-Mitt.
46
13-47
CA: 96: 154562d

78. Dietze, H. J. and Zahn, H.
1981
Mass spectrometric analysis of calcium fluoride single crystals
ZfI-Mitt.
46
60-8
CA: 96: 154564f

79. Jochum, K. P., Seufert, M., and Knab, H. J.
1981
Quantitative multielement analysis of geochemical and cosmochemical samples using spark source mass spectrometry
Fresenius' Z. Anal. Chem.
309(4)
285-90
CA: 94: 76159v

80. Knab, H. and Hintenberger, H.
1980
Determination of 20 trace elements in geologic samples by isotope dilution method combined with spark source mass spectrography
Anal. Chem.
52(3)
390-4
CA: -

81. Kodama, T., Kadowaki, S., and Oda, H.
1978
Determination of elements in environmental samples by spark source mass spectroanalysis
Aichi-ken Kogai Chosa Senta Shoho
6
125-8
CA: 91: 95841r

82. Matteucci, E. and Restivo, G.
1983
Determination of 61 elements in silicate samples by spark source mass spectrometry
Rend. Soc. Ital. Mineral. Petrol.
1982 38(3)
1281-5
CA: 101: 103127e

83. Pimminger, M., Grasserbauer, M., Schroll, E., and Cerny, I.
1983
Trace analysis of microareas of geologic samples by SIMS
Fresenius' Z. Anal. Chem.
316(3)
293-8
CA: 99: 205229x

84. Sanderson, T. K., Mapper, D., and Farren, J.
1984
The determination of trace elements in solid samples by laser source mass spectrometry
U. K. At. Energy Res. Establ. [Rep.] AEREGR
AERE-R 11113
32 pp.
CA: 101: 103137h

85. Vandelanoote, R., Blommaert, W., Gijbels, R., and Van Grieken, R.
1981
Analysis of geothermal samples by spark source mass spectrometry
Fresenius' Z. Anal. Chem.
309(4)
291-4
CA: 96: 74364a

86. Argollo, R. M. and Schilling, J. G.
1978
Simultaneous determination of gallium and germanium in igneous rocks by neutron activation
Anal. Chim. Acta
96(1)
117-23
CA: -

87. Asaragov, Kh. B. and Toichkin, A. N.
1985
Neuton activation determination of heavy elements in environmental media of the Kola peninsula
Yad.-Fiz. Metody Anal. Kontrole Okruzh, Svedy, Tr. Vses. Soveshch,
2nd 1982
189-92
CA: 103: 134104r

88. Barrandon, J. N., Borderie, B., Halfon, J., Marce, A., and Melky, S.
1977
Methodology of analysis using californium-252 for application to the earth sciences and particularly mining research
Ext. Abstr. - Int. Symp. Anal. Chem. Explor. Min. Process. Mater.
1976
229-34
CA: 89: 225601j

89. Berthelot, C., Carraro, G., and Verdingh, V.
1980
Nondestructive multielement photon activation analysis of river sediments
J. Radioanal. Chem.
60(2)
435-41
CA: 94: 76129k

90. Delmas, R., Barrandon, J. N., and Debrun, J. L.
1976
Trace analysis of various minerals using 10 MeV proton acivation and direct gamma spectrophotometry. A comparison with thermal NAA
Analusis
4(8)
339-46
CA: 86: 50270j

91. Gharib, A. and Morris, D. F. C.
1980
Determination of germanium and tin in geological materials by radiochemical neutron activation analysis
Radiochem. Acta
27(1)
35-8
CA: 92: 157234b

92. Kolesov,, G. M., Zaslavskaya, N. I., Mastalka, A., and Frana, J.
1982
Determination of trace element content in iron meteorites by the neutron-activation method using a shuttle
Meteoritika
40
45-8
CA: 98: 6638j

93. Kraehenbuehl, U. and Wegmeuller, F.
1978
Determination of volatile trace elements in terrestrial minerals and lunar soils by RNAA
Radiochem. Radioanal. Lett.
36(1)
31-9
CA: -

94. Kueppers, G. and Erdtmann, G.
1981
Method for determining trace elements in water samples using neutron activation analysis
Ber. Kernforschungsanlage Juelich
Juel-1716
94pp.
CA: 95: 156229d

95. Lebedev, A. K.
1981
Determination of germanium in coals by an x-ray radiometric method
Metody Razved. Geofiz. Yader Geofiz. v Rud. Geol.
L. 1981
49-54
from Ref. Zh., Geol. 1982
Abstr. No. 6K321
CA: 97: 130302p

96. Ruch, R. R., Cahill, R. A., Frost, J. K., Camp, L. R., and Gluskoter, H. J.
1977
Survey of trace elements in coals and coal-related materials by neutron activation analysis
J. Radioanal. Chem.
38(1-2)
415-24
CA: 87: 170225r

97. Shima, M., Yabuki, S., Kimura, T., and Yabuki, H.
1981
A revised method for the determination of major and trace elements in iron meteorites by neutron activation analysis
Bull. Natl. Sci. Mus., Ser. E (Tokyo)
4
193-6
CA: 97: 103507c

98. Sundberg, L. L. and Boynton, W. V.
1977
Determination of ten trace elements in meteorites and lunar materials by radiochemical neutron activation analysis
Anal. Chim. Acta
89(1)
127-40
CA: -

99. Torgov, V. G., Yatsenko, V. T., Gil'bert, E. N., and Nikitin, V. N.
1980
Extraction-neutron-activation method for simultaneous determination of arsenic and germanium in ores and products of their processing
Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim. Nauk
(4)
108-14
CA: 93: 160650k

100. Braungart, M. and Ruessel, H.
1984
Separation of molydoheteropoly acids of phosphorus, arsenic, silicon and germanium as ion-associates by HPLC. Application to quantitative determination in water
Chromatographia, 19
185-7
CA: 102: 225730m

101. Chang, C. and Hsueh, H.
1980
Catalytic polarograms of germanium-pyrogallol-hydrogen peroxide system
Fen Hsi Hua Hsueh
8(1)
33-8
CA: 94: 57436s

102. Chaudhuri, M. K., Das Gupta, H. S., and Khathing, D. T.
1979
North-east Indian coal. An assessment of its potential as a germanium source
Chem. Ind.
(14)
475-6
CA: 92: 25291h

103. Isaeva, K. G. and Viktorova, M. E.
1983
Separation of germanium from accompanying elements by paper chromatography
Zh. Anal. Khim.
38(5)
944-6
CA: 99: 63391t

104. Lagunov, M. D. and Pichugina, A. P.
1983
Determination of germanium in manganese-activated zinc magnesium germanate (Zn,Mg)2(Si,Ge)04 luminophor
Sb. Nauchn. Tr.-Vses. Nauchno-Issled. Inst. Lyuminoforov Osobo Chist. Veshchestv. 25
109-11
CA: 102: 38929x

105. Lu, K.
1984
Polarographic adsorption catalytic wave of germanium and its application in germanium determination in ores
Yanshi Kuangwu Ji Ceshi
3(1)
292-5
CA: 101: 182833h

106. Mirzoyan, F. V., Tarayan, V. M., and Dzhrbashyan, A. E.
1982
Determination of germanium
from Otkrytia Izobret., Prom. Obratzsy, Tovarnye Znaki
(46)
207
CA: 98: 154657e

107. Tuan, H., Wang, H., and Yang, Y.
1978
Polaroagraphic determination of small amount of germanium in minerals
Fen Hsi Hua Hsueh
6(6)
486
CA: 92: 103743y

108. Wei, X.
1982
Polarographic catalytic wave of germanium and its application in ore analysis
Fenxi Huaxue
10(4)
193-6
CA: 97: 192424p

109. Abbey, S., McLeod, C. R., and Wan, L. G.
1983
Fe-R1, Fe-R2, Fe-R3 and Fe-R4: four Canadian iron formation samples prepared for use as reference materials
Pap. Geol. Surv. Can.
83-19
54pp.
CA: 99: 132955u

110. Bernstein, L. R.
1985
Germanium geochemistry and mineralogy
Geochim. Cosmochim. Acta
49
2409-22
CA: -

111. De la Roche, H. and Govindaraju, K.
1976
New geochemical standards: granite GS-N and feldspar FK-N
Analusis
4(8)
347-72
CA: 86: 50177j

112. Dixon, K.
1978
An evaluation of the methods used at the National Institute of Metallurgy for the analysis of base-metal concentrates
Natl. Inst. Metall., Repub. So. Africa Rep.
1963
12pp.
CA: 89: 122547s

113. Gindy, A. R., El-Askary, M. A., and Khalil, S. O.
1978
Differential thermal and thermogravimetric studies and some trace-element contents of some coals and carbonaceous shales from west-central Sinai, Egypt
Chem. Geol., 22(4)
267-83
CA: -

114. Henderson, J. A. Jr., Oman, C. S., and Coleman, S. L.
1981
Analysis of coal samples collected 1975-1977
Va. Div. Miner. Resour. Publ.
33
135pp.
CA: 96: 55050d

115. Henry, W., M., Mitchell, R., I., and Knapp, K. T.
1978
Inorganic compounds present in fossil fuel fly ash
EPA Off. Res. Dev., EPA 1978
EPA 600/9-78-020b
PB-237, 437
185-207
CA: 91: 95921s

116. Kati, O.
1983
Concentration of some trace elements during processing of copper-bearing ores
Shkencave Nat.
37(3-4)
85-8
CA: 103: 40353u

117. Nadkarni, R. A.
1982
Comprehensive elemental analysis of coal and fly ash
ACS Symp. Ser.
205
147-62
CA: -

118. Novikov, N. A., Ruzankin, V. I., Samoilova, V. F., Zakrevskaya, T. M., Nazirmadov, B., and Shchekoturova, E. K., 1980
Determination of microamounts of vanadium, molybdenum, iron, chromium, and germanium in a saturated sodium chloride solution
Issled. v Obl. Neorg. Khimii Razdelenie, Konsentrironvanie i Analiz Neorg. Veshchestv, Dushanbe
61-6
from Ref. Zh. Khim.
Abstract No. 20G214
CA: 96: 45499t

119. Polotebnova, N. A. and Krachun, S. V.
1982
Heteropoly compounds as reagents in analytical chemistry
Dep. Doc. 25 SPSTL 71 KhP-D82
25pp.
CA: 98: 190687y

120. Weber, P. N., ed.
1973
Geochemistry of germanium
Benchmark Papers in Geology Series
466 pp.
Dowden, Hutchinson, and Ross
Stroudsburg, PA
CA: -

121. Xie, X., Yan, M., Li, L., and Shen, H.
1985
Geochemical reference samples, GSD 1-8 from China
Geostand. Newsl.
9(1)
83-159
CA: -

122. Yushkova, G. E. and Antonova, L. A.
1981
Determination of elements in sulfides
Tr. In-t Geol. Komi Fil. AN SSSR
(36)
51-3
from Ref. Zh., Geol. 1982
Abstr. No. 8V645
CA: 97: 207293w

123. Abbey, S.
1983
Studies in "standard samples" of silicate rocks and minerals
Pap. Geol. Surv. Can.
83-15
114 pp.
CA: -

124. Antonovich, V. P., Suvarova, E. N., Golik, N. N., and Nazarenko, V. A.
1985
Selective photometric determination of germanium with tetrabromosalicyl-
fluorone
Zh. Anal. Khim.
40(5)
834-9
CA: 103(18): 152794v

125. Govindaraju, K.
1984
1984 compilation of working values for 170 international reference samples
of mainly silicate rocks and minerals
Geostand. Newsl.
8 (Special Issue)
CA: -

126. Kolb, A., Muller-Vogt, G., and Wendl, W.
1987
Chemical reactions in the determination of germanium by graphite furnace
atomic absorption spectrometry
Spectrochim. Acta
42B(8)
951-7
CA: -

127. Kunc, S. and Necipoglu, Z.
1987
Determination of germanium in Turkish coals by GFAAS
Doga: Kim. Ser.
11(1)
22-6
CA: 107(8): 61738w

128. Lu, K.
1984
Polarographic adsorption catalytic wave of germanium and its application in germanium determination in ores
Yanshi Kuangwu Ji Ceshi
2(4)
292-5
CA: 105: 145302w (see CA 101:182833h)

129. Marczenko,Z., Krasienko, M., and Klebek, A.
1986
Spectrophotometric determination of germanium based on its ternary complex with phenyfluorone and zephiramine
Microchem. J.
34(1)
121-6
CA: 105: 126249t

130. Mehta, Y. L., Bhanawat, S. C., and Mehta, S. C.
1985
A rapid spectrophotometric method for the estimation of germanium in zinc concentrate, zinc oxide and drum filter cake
Indian J. Chem.
24A(11)
985-6
CA: 104: 141266u

131. Nazarenko, V. A., Antonovich, V. P., Suvorova, E. N., and Golik, N. N.
1984
Tetrabromosalicylfluorone - a novel selective reagent for photometric determination of germanium
Dopov. Akad. Nauk Ukr. RSR, Ser. B: Geol., Khim. Biol. Nauki
10
44-6
CA: 102(6): 55209e

132. Schery, S. D.
1985
New capabilities for the measurement of natural radioactivity using low energy photons
Occup. Radiat. Saf. Min., Proc. Int. Conf., J. Stocker, (Ed.)
2
381-5
CA: 104: 137888f

133. Shen, H., Wang, Z., and Xu, G.
1987
Spectrophotometric determination of trace amounts of germanium in minerals and ores with 9-(o-chlorophenyl-2,6,7-trihydroxyxanthen-3-one in the presence of cetyltrimethylammonium bromide
Analyst (London), 112(6)
887-9
CA: 107: 69837r

134. Watanabe, K., Sasaki, K., Imai, S., and Omura, Y.
1986
Determination of trace germanium in silicate rocks
Ryusan To Kogyo
39(10)
138-42
CA: 106: 112785r

135. Xi, G. and Liang, D.
1986
Spectroscopic determination of germanium using 2,4-dichlorophenylfluorone-cetyltrimethylammonium bromide
Fenxi Huaxue
14(4)
284-5
CA: 105: 145171c

136. Xia, J., Zhang, W., and Li, S.
1986
Microdetermination of germanium in water
Huanjing Huaxue
5(6)
43-7
CA: 107(4): 28088m

137. Zhang, J., Liu, X., and Song, J.
1985
Determination of germanium in geological samples by graphite furnace AAS (atomic absorption spectroscopy) using a mixed matrix modifier
Yanshi Kuangwu Ji Ceshi
4(4)
350-4
CA: 104: 179296s