

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/23429437>

Determination of iron in silicate rocks by substoichiometric radioisotope dilution analysis

ARTICLE *in* TALANTA · FEBRUARY 1976

Impact Factor: 3.55 · DOI: 10.1016/0039-9140(76)80008-2 · Source: PubMed

CITATIONS

7

READ

1

2 AUTHORS, INCLUDING:



[Eiliv Steinnes](#)

Norwegian University of Scienc...

529 PUBLICATIONS **10,789**

CITATIONS

SEE PROFILE

Table 1. Some characteristics of the programs COMICS, EQUIL, DISDI and DISDI* used on a CDC 6600 computer

Program	S	Tco	Tca	M	D	M-D
COMICS	176	1.2	170	19.2	9.6	9.6
EQUIL	429	2.6	80-190	14.8	4.1	9.6
DISDI	154	1.2	100	9.3	0.3	9.0
DISDI*	237	1.6	135	17.0	7.6	9.4

S: number of cards. For the program COMICS and EQUIL there is a little difference from the original number, but only in the data input.

Tco: compilation time, sec.

Tca: calculation time referred to the program DISDI (= 100).

M: total number of memories (K storage locations) required for the programs in the version used.

D: total number of memories required by dimensions assigned to the variables.

M - D: difference between the total memories and those required by dimensions assigned to the variables. This parameter is more significant than either D or M because the dimensions can be easily varied according to the requirements of the program user.

than COMICS for most of the points, and although EQUIL converged faster, the calculation time was not lower. Table 1 gives some data for DISDI, DISDI*, COMICS and EQUIL.

In testing the program DISDI*, the dimensions used for the distribution diagrams were 32×23 cm, but were later reduced to 25×17 cm, which is sufficient in most cases. If the iterative process is stopped when the differences $M - M_{calc}$, $A - A_{calc}$ and $B - B_{calc}$ are less than 0.01% (and not 0.001% as for the data reported in Table 1) the number of iterations and hence the calculation time is reduced by 20-60%, with a difference of 0.001, at most, in $-\log C_j$.

DISDI is simple to use, does not greatly encumber the computer memory and is rapid. The more complex version, DISDI*, has the advantage of giving immediate representation of the species distribution in the system considered.

The complete listing of the program DISDI* is available from the authors on request.

Acknowledgements—We thank Dr. C. Rigano for the valuable advice he has given us in developing the programs, and the C.N.R. for financial support.

REFERENCES

1. N. Ingri, W. Kakolowicz and L. G. Sillén, *Talanta*, 1967, **14**, 1261.
2. D. D. Perrin and I. G. Sayce, *ibid.*, 1967, **14**, 833.
3. Ting-Po I and G. H. Nancollas, *Anal. Chem.*, 1972, **44**, 1940.

Summary—A simple computer program (DISDI) has been developed for obtaining the distribution diagrams of the species in solutions containing up to one metal and two ligands. It has been compared with the programs COMICS and EQUIL.

DETERMINATION OF IRON IN SILICATE ROCKS BY SUBSTOICHIOMETRIC RADIOISOTOPE DILUTION ANALYSIS

E. GUNDERSEN and E. STEINNES

Institutt for Atomenergi, Isotope Laboratories, Kjeller, Norway

(Received 5 February 1975. Accepted 16 April 1975)

Although substoichiometric isotope dilution analysis is considered most useful at trace element levels, it can also be advantageously used for the precise determination of major components.¹ This is so because the two most important factors for the overall precision of such a method, i.e., the reproducibility of the substoichiometric separation and the counting statistics, may both be kept at a very low variability where relatively large amounts of an element are to be determined. In a previous work by the authors² it was shown that the determination of iron in biological reference materials could be carried out with high precision at the concentration levels concerned. It was decided to

see whether a similar method could be used for the determination of the total concentration of iron in rocks with satisfactory precision and accuracy.

The method for biological material is based on wet-ashing of the sample with nitric acid and sulphuric acid and subsequent extraction of iron from 3M sodium chloride medium and back-extraction with dilute nitric acid. A procedure similar to that of Stary and Růžička³ is then followed. A substoichiometric amount of EDTA is added, and the solution is applied to a cation-exchange column, where the excess of iron is retained, while the Fe(III)-EDTA complex passes through quantitatively.

Table 1. Concentration of iron in five U.S. Geological Survey standard rocks, determined by substoichiometric radioisotope dilution (% Fe)

	Andesite AGV-1	Basalt BCR-1	Granite G-2	Granodiorite GSP-1	Diabase W-1
	4.71	9.30	1.89	3.00	7.78
	4.71	9.39	1.90	2.95	7.80
	4.72	9.28	1.91	3.01	7.83
	4.71	9.43	1.88	3.00	7.87
	4.79	9.31	1.95	3.00	7.80
	4.81	9.32	1.92	3.01	7.85
Mean value	4.74	9.34	1.91	3.00	7.82
Relative standard deviation, %	0.97	0.62	1.26	0.78	0.45
Expressed as % Fe_2O_3 Johansen and Steinnes, ⁴ neutron activation	6.78	13.35	2.73	4.29	11.18
Fleischer, ⁵ recommended value	6.75	13.40	2.65	4.31	11.12
Flanagan, ⁶ average value	6.80	13.51	2.77	4.33	11.09

After some preliminary experiments it appeared that the method, with some small modifications, could be applied to the determination of total iron in rocks after hydrofluoric acid dissolution of the sample.

EXPERIMENTAL

Apparatus

Counting equipment. A scintillation counter with a 75 × 75 mm NaI(Tl) crystal.

Cation-exchange columns. Tubes of 12 mm internal diameter filled with Dowex 50W-X8, 100–200 mesh, Na^+ -form, to give a 50-mm height of resin bed. The column is prepared by treating the resin in the H^+ -form with an excess of 1M sodium hydroxide and washing with water until the eluate is neutral.

Reagents

The reagents used were *pro analysi* grade.

EDTA solution. Prepared by dissolving the disodium salt of EDTA in water. The solution was standardized against Fe(III) solutions of known concentration, according to the substoichiometric procedure given below.

^{59}Fe tracer. A solution of specific activity 3000 mCi/g was diluted with 0.1 M hydrochloric acid to a concentration of about 1 $\mu\text{Ci/ml}$.

Boric acid solution, 30 mg/ml.

Procedure

Weigh accurately about 50 mg of finely divided rock powder into a 100-ml Teflon beaker. Add 10 ml of concentrated hydrofluoric acid, 2 ml of concentrated nitric acid and 1.00 ml of ^{59}Fe tracer solution. Evaporate the mixture to complete dryness on a hot-plate. Then add 5 ml of 6M hydrochloric acid and 1 ml of boric acid solution and evaporate to dryness again. Dissolve the residue in 5 drops of concentrated nitric acid and 15 ml of 4M sodium chloride, then extract with 15 ml of isopropyl methyl ketone. Back-extract the iron with 15 ml of 0.01M nitric acid. To the resulting solution add a known volume of EDTA solution corresponding stoichiometrically to an amount of iron (y) which is about 60% of the estimated amount of iron in the sample (1 molecule of EDTA corresponds to 1 atom of Fe).

Allow the solution to stand for 10–15 min at 30–40°, and then pass it through the cation-exchange column

(flow-rate about 0.5 ml/min), taking care to transfer the solution quantitatively to the column. Wash the column with two 5-ml portions of water. Measure the activity of the combined eluates (A_s) with the scintillation counter, and the activity of 1.00 ml of ^{59}Fe tracer solution diluted to the same volume (activity A_t). Calculate the amount of iron (x) present in the sample from the relationship $x = y A_t / A_s$.

The reagent blank, determined in the same way as described above, was found to be insignificant when working in the concentration range in question.

RESULTS AND DISCUSSION

The method was tested on five U.S. Geological Survey standard rocks with composition ranging from basaltic to granitic and with iron contents in the range 1.9–9.3%. These standard rocks have been analysed in many laboratories by a variety of analytical techniques, and their iron contents can be assumed to be well known. Before this work the same rocks were analysed in the authors' laboratory by a radiochemical neutron-activation method⁴ assumed to yield results of high accuracy. A comparison of the results obtained by substoichiometric isotope dilution with the literature values is given in Table 1. The agreement with the recommended values is within 1.5% relative in all cases. A similarly good agreement is evident with the work of Johansen and Steinnes,⁴ except in the case of G-2 where the neutron-activation values seem to be about 3–4% low.

The good agreement with the literature values seems to indicate that no significant systematic errors were present in the analyses. The relative standard deviation is about 0.5–1% for iron contents exceeding 3%. This implies that the quality of data obtained by the substoichiometric isotope dilution method described in this work would be as good as that of most data produced by the conventional methods of rock analysis. The present method may not be well suited for routine analyses, but could be a useful supplement in cases where the results obtained by other methods are to be checked.

REFERENCES

1. L. T. McClendon, *Technical Note* 501, p. 113. U.S. Department of Commerce, National Bureau of Standards, 1970.

2. E. Gundersen and E. Steinnes, *Talanta*, 1971, **18**, 1167.
3. J. Starý and J. Růžička, *ibid.*, 1961, **8**, 775.
4. O. Johansen and E. Steinnes, *ibid.*, 1970, **17**, 407.
5. M. Fleischer, *Geochim. Cosmochim. Acta*, 1969, **33**, 65.
6. F. J. Flanagan, *ibid.*, 1969, **33**, 81.

Summary—Iron is determined in rocks by an isotope dilution method involving dissolution with hydrofluoric acid, extraction of iron(III) chloride into isopropyl methyl ketone, stripping with dilute nitric acid, and substoichiometric separation of the Fe-EDTA complex on a cation-exchange column. The precision and accuracy are 1.5% relative or better, as indicated by analyses of some U.S. Geological Survey standard rocks.

Talanta, Vol. 23, pp. 46-47. Pergamon Press, 1976. Printed in Great Britain

SEQUENTIAL DETERMINATION OF THORIUM AND RARE EARTHS WITH EDTA AND KOJIC ACID

S. Y. SHETTY and R. M. SATHE

Analytical Chemistry Division, Bhabha Atomic Research Centre, Modular Labs.,
Trombay, Bombay-400085, India

(Received 23 January 1975. Accepted 20 April 1975)

The significant differences in the stabilities of the EDTA complexes of thorium and the rare earth metals can, in principle, be exploited for sequential determination of these ions. Thorium can be conveniently titrated at pH 2.0 followed by the rare earths at pH 5.5. Such a procedure, however, meets with difficulty in practice. The indicator suitable for this pH range is Xylenol Orange (XO). The free indicator is lemon-yellow and its complexes red-violet. After the initial titration of thorium, however, the Th-EDTA complex produces a pink colour when the pH is raised to 5.5, thus making titration of the rare earths impossible. Přibil and Veselý¹ ascribed this colour to the formation of a ternary complex Th-EDTA-XO and suggested the use of excess of acetylacetone to prevent its formation so that the rare earths could be titrated. We have found kojic acid to be a similar masking agent for this purpose and its use is described in this note. Though the use of ligands such as DTPA or TTHA obviates the need for such a masking agent, the ready availability of EDTA makes its use still attractive.

EXPERIMENTAL

Reagents

Rare earth solutions. Rare earth metal oxides (purity $\geq 99.9\%$) were dissolved in nitric acid and the solutions standardized by EDTA titration with hexamine as buffer and XO as indicator.

Thorium solution. Thorium nitrate ($\geq 99.9\%$) was dissolved and the solution standardized with EDTA.

Xylenol Orange. A freshly prepared 0.5% solution of sodium salt in water.

Kojic acid. The BDH (biochemical grade) product was recrystallized from alcohol (with animal charcoal added) to give buff needles.

All other reagents were analytical grade.

Procedure

Dilute the sample solution containing about 10 mg of thorium and 50-60 mg of rare earth metals to about 200 ml

and adjust the pH to 1.9-2.0 with ammonia or nitric acid, using a pH-meter. Add a few drops of XO and titrate slowly with 0.05M EDTA till the colour changes from pink to lemon-yellow. Add kojic acid (solid) equivalent to about ten times the thorium content and stir well to dissolve it. Raise the pH to 5.5 (pH paper) with a saturated solution of hexamine. Titrate further with 0.05M EDTA till the pink colour again completely changes to yellow.

Analysis of monazite. Isolate thorium and rare earth metals from the sample as oxalates by the method of Schoeller and Powell.² Carefully ignite to the oxides at 650-700°, dissolve these in hydrochloric acid (to keep cerium in the 3+ state) and make up to standard volume. Titrate a suitable aliquot as above.

RESULTS AND DISCUSSION

Our potentiometric studies on mixed-ligand chelates of thorium have revealed that kojic acid forms a colourless ternary complex with Th-EDTA at a pH as low as 4.5, and can be used to suppress the formation of the pink Th-EDTA-XO chelate. If kojic acid is added after the first end-point, sequential titrations of mixtures containing different amount of Th⁴⁺ and Ln³⁺ can be successfully accomplished (Table 1).

The advantage of kojic acid over acetylacetone is its higher solubility in water and thus it can be used for higher concentrations of thorium. The colour change is quite sharp and no heating is necessary as in the case of acetylacetone. However, the heavier rare earths, if present in amounts higher than that of thorium, have been found to interfere in the thorium determination. The method has been found to work successfully for monazite, which mainly contains lanthanum, cerium, neodymium and praseodymium, the validity being established by titration of a second aliquot of solution with DTPA for comparison.

Acknowledgement—Our thanks are due to Dr M. Sankar Das, Head, Analytical Chemistry Division, for his help and keen interest in the work.