



ELSEVIER

Journal of Chromatography A, 770 (1997) 93–98

JOURNAL OF
CHROMATOGRAPHY A

Determination of chlorine and bromine in rocks by alkaline fusion with ion chromatography detection

P.A. Blackwell^{a,*}, M.R. Cave^a, A.E. Davis^a, S.A. Malik^b

^aAnalytical Geochemistry Group, British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK

^bPostgraduate Research Institute for Sedimentology, University of Reading, Whiteknights, Reading, RG6 6AJ, UK

Abstract

This study describes the use of alkaline fusion by sodium peroxide to dissolve chlorine and bromine in rocks to produce a solution which, with appropriate pre-treatment, is suitable for analysis by ion chromatography. Results are given for a selection of sedimentary and igneous rocks. The accuracy of the fusion method is evaluated by analysis of Geological Survey of Japan reference materials. Additionally, a spike recovery test is performed to show that the fusion process is quantitative for chlorine and bromine. The results for chlorine are in the range 58–3860 mg kg⁻¹ and show good agreement both with results obtained by pyrohydrolysis with flow injection colorimetric detection and results obtained by aqueous leaching of the samples with ion chromatography detection. Results for bromine are in the range <3–4.5 mg kg⁻¹. Because of the relatively few data obtained in this study and the relative paucity of published data for reference materials, an assessment of the accuracy of the fusion method for bromine is more difficult. The limits of detection for this method are 36 and 3 mg kg⁻¹ for chlorine and bromine, respectively.

Keywords: Chlorine; Bromine

1. Introduction

This study seeks to develop a rapid, quantitative method for the determination of chlorine and bromine in rock samples in order to assist hydro-geochemical modelling. Chlorine and bromine are considered to be conservative elements in ground-water systems and, therefore, their concentration in pore-waters can be a useful tool in constraining the origins of groundwater salinity. Whole rock determinations for chlorine and bromine are therefore important in helping to distinguish between saline intrusions and palaeosalinity, for example.

Several analytical techniques have been used for the determination of halogens in rocks; neutron

activation analysis [1,2] and X-ray fluorescence spectrometry [2] may be applied directly to solids; mass spectrometry [3,4], ion selective electrode [5], colorimetry [6] and ion chromatography [3] are techniques that require a preparation stage, e.g. acid digestion [7] or pyrohydrolysis [3,8], to obtain a solution for analysis. Factors such as availability of equipment, speed, simplicity, accuracy, precision and limits of detection all influence the choice of analytical technique. In this study, ion chromatography, which is commonly used for sensitive, simultaneous anion determination in many laboratories, was a convenient and practical method of detection. For this technique, it is essential to render the sample into a non-acidic solution first and alkaline fusion [1] was a convenient and practical method of preparing such a solution. The data obtained were compared

*Corresponding author.

with those from an independent method, that of pyrohydrolysis with colorimetric detection, in order to provide additional comparative data because of the relative paucity of chlorine and bromine data for the two reference materials analysed. Also, the samples were leached with deionised water and analysed by ion chromatography to provide estimates of the halogen contribution from water-leachable pore-water evaporites precipitated during drying of the rock. In this study, eight rock samples were analysed: two sandstones; two breccias; three igneous volcanic rocks and a carboniferous limestone, together with two igneous reference materials from the Geological Survey of Japan (GSJ): JR-1, a rhyolite, and JB-2, a basalt.

2. Experimental

2.1. Reagents

All reagents and standards used were of analytical grade (Merck, Lutterworth, UK). The working standard and spiking solutions were prepared by dissolving sodium and potassium salts in 18 M Ω deionised water (Elga, High Wycombe, UK).

2.2. Sample preparation

The rocks were cylindrical drill core samples, approximately 8 cm in diameter and 50 cm total length. The end 2–5 cm and the outer 2 cm annulus of the drill core were removed by a mechanical splitter to minimise any possible contamination of the core from the drilling fluid used during drilling. The trimmed core material was crushed using a mechanical jaw crusher, dried at 40°C for 24 h, and then sieved to remove the <180 μ m fraction. The >180 μ m fraction was milled to <350 μ m using a tema mill and the two size fractions were recombined to produce the prepared core sample.

2.3. Pyrohydrolysis

This method has been described in detail by Whitehead and Thomas [8]. For preparation of a solution suitable for chlorine analysis, 0.1–0.2 g of the prepared core material or reference material was

weighed into a clean and dry quartz boat, and 0.6 g of vanadium pentoxide was added. The mixture was reacted at 1230°C for 15 min with a steam–air carrier gas flowing over the sample at 3.3 ml min⁻¹ to sweep the evolved gaseous hydride into a mixed 0.2 M sodium hydroxide and 0.02 M sodium acetate absorbing solution. For preparation of a solution suitable for bromine analysis, 0.5 g of the prepared core material or reference material and 2.5 g of vanadium pentoxide were used with a reaction temperature of 1060°C and an absorbing solution of 0.01 M sodium hydroxide. The solutions were made up to volume quantitatively with deionised water.

2.4. Aqueous leaching

A 5-g amount of the prepared core material or reference material was weighed into a clean and dry centrifuge tube, 30 ml of deionised water were added and the mixture was shaken for 24 h. The mixture was then centrifuged at 15 485 g for 15 min and the supernatant solution was filtered to 0.45 μ m using a nylon filter disk (Gelman Sciences, Northampton, UK).

2.5. Alkaline fusion

A 0.25-g amount of the prepared core material or reference material was weighed into a clean and dry zirconium crucible, 2 ml of a 1-M sodium hydroxide solution were added and the mixture was evaporated to dryness at 125°C. A 1.4-g amount of sodium peroxide was then added and the mixture was fused over a low heat for 5 min, ensuring that the temperature did not exceed a dull red heat (approximately 650–700°C). Keeping the temperature low in this manner ensures that the sodium peroxide does not decompose before reacting with the rock. After 5 min, the temperature was allowed to rise above a dull red heat in order to destroy most of the remaining sodium peroxide. The crucible was then allowed to cool, rotating the crucible initially to spread out the fusion cake to assist the aqueous leaching. After 5 min, whilst the crucible was still warm, approximately 15 ml of deionised water were added to leach the fusion cake and destroy any remaining sodium peroxide. The fusion cake was leached for 30 min and any remaining fusion cake

was broken up with a PTFE rod. The contents of the crucible were then transferred to a plastic volumetric flask, with washings, and made up to a total volume of 50 ml with deionised water. The solution was shaken well and allowed to settle overnight.

2.6. Solution pre-treatment

The solution obtained from the alkaline fusion contains approximately 0.75 M sodium hydroxide. It is thus unsuitable for direct analysis by ion chromatography because of the high content of total dissolved solids, which may cause column overloading. In addition, the high hydroxide concentration will act as an eluent, modifying retention times and appearing as a large analytical peak, which may mask other analytical peaks. The solution was therefore pre-treated using Dionex (Sunnyvale, CA, USA) on-guard H cartridges (part No. 039596). These contain a protonated ion-exchange resin that will exchange cations from the solution with protons, thus both neutralising the solution and lowering the content of dissolved solids in the solution. The cartridges were initially flushed with 2 ml of deionised water, before 5 ml of alkaline fusion solution were passed through the cartridge; the initial 3 ml of treated solution were discarded and the flow-rate through the cartridge did not exceed 2 ml min⁻¹. Because the capacity of the cartridges is reported to be equivalent to 10 ml of 0.2 M sodium hydroxide solution, two cartridges were required for each neutralisation. After aliquots had been collected for analysis, the pH of the next drop of solution was measured with universal indicator paper to ensure that the cartridges had not been exhausted during the neutralisation.

2.7. Analysis

Chlorine analysis of the pyrohydrolysis solution was performed colorimetrically, using mercuric thiocyanate colour reagent as described by Zall et al. [9], on a Technicon (Tarrytown, NY, USA) AutoAnalyser II system fitted with a chloride manifold. The colorimeter was fitted with a 15-mm flow through cell and 480 nm filters. Bromine analysis of the pyrohydrolysis solutions and all other analyses were performed on a Dionex 2000i ion chromatograph with autosampler. A 50- μ l volume of the sample was

injected into the mobile phase. Separations were performed with an Ionpac AG12A guard column and an AS12A analytical column with a mixed eluent of 2.7 mM sodium carbonate and 0.3 mM sodium hydrogencarbonate, which was pumped isocratically at 1.5 ml min⁻¹. Chloride was detected by suppressed conductivity detection and bromide was simultaneously detected using a flow through Phillips (Cambridge, UK) PU4110 UV detector at 210 nm.

3. Results and discussion

Results are quoted with errors based on one standard deviation of the data.

3.1. Fusion blanks

An empty zirconium crucible was taken through the fusion process in the same manner as that used for the samples. The fusion solution produced was treated and analysed in the same manner as the samples. Chlorine was detected in this solution (Fig. 1) and therefore all analytical results were blank corrected. The source of the chlorine is likely to be the reagents used. Bromine was not detected in the blank (Fig. 2).

3.2. Analysis of reference materials

Results and reference values for reference materials analysed by both fusion-ion chromatography (IC) and pyrohydrolysis-colorimetry are summa-

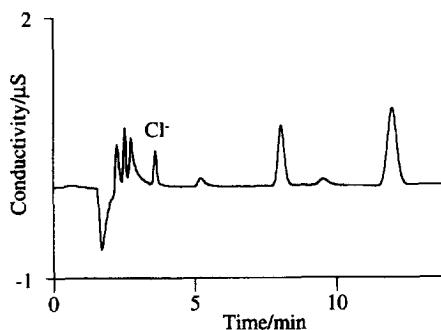


Fig. 1. Chromatogram of the fusion blank showing the chloride peak successfully resolved from matrix components (suppressed conductivity detection).

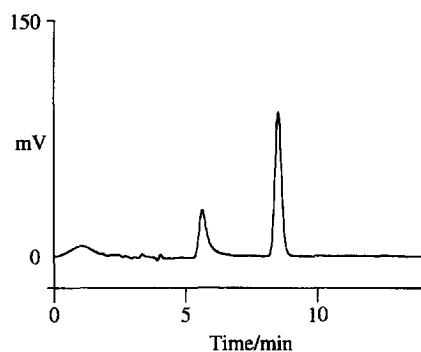


Fig. 2. Chromatogram of the fusion blank showing the lack of the bromide peak which would elute at 7.3 min (UV detection at 210 nm with f.s.d. at 1 V).

rised in Table 1. It can be seen that chlorine data achieved for the two reference materials by fusion-IC agree, within the uncertainty, with the quoted values [10]. Only one and two determinations, respectively, are available for bromine in JB-2 and JR-1 and so the individual results, which are guide values and not reference values, are included without errors. The bromine result for JR-1 falls between the two published results and although bromine was not detected in JB-2, there is only one published result

with which to compare it. The relative lack of bromine data is discussed later.

3.3. Spike recoveries

A mixed chloride and bromide solution was prepared with a chloride-bromide concentration ratio of 10:1 and this was used to spike JB-2, prior to the alkaline fusion stage, at four different concentrations. This concentration ratio was chosen for convenience. In a selection of igneous GSJ reference materials, the chlorine-bromine ratios lie in the range 6.1–7250 [10]. Recoveries in the range 80–145% for chlorine and 94–128% for bromine were achieved. The spike levels and fusion-IC data are summarised in Table 2 and show that the recoveries for chlorine and bromine are quantitative (see Figs. 3 and 4).

3.4. Comparison of data obtained by three independent methods

The main methodological difference between fusion and pyrohydrolysis is the temperature of the reaction. Pyrohydrolysis is carried out at higher temperatures, e.g. 1030–1230°C, in order to drive off the halogens as acid vapours, which are then collected in alkaline solution. Alkaline fusion, on the

Table 1

Chlorine and bromine data (in mg kg⁻¹) obtained for GSJ reference materials, JR-1 and JB-2, by fusion-IC and pyrohydrolysis-colorimetry (Cl) and IC (Br)

	Chlorine			Bromine		
	Reference	Fusion	Pyrohydrolysis	Guide	Fusion	Pyrohydrolysis
JB-2	281±58	247±11	267±11	6	<3	<6
JR-1	920±81	891±32	817±10	2,10	4.7±1.3	<6

Table 2

Recovery data (in µg) expressed as a percentage for chloride and bromide spikes of JB-2

Chloride			Bromide		
Spike	Analysed	Recovery (%)	Spike	Analysed	Recovery (%)
50	49±9	80–116	5	5.9±0.5	108–128
100	119±26	93–145	10	11.4±1.4	100–128
200	201±3	99–102	20	19.5±0.3	96–99
500	496±3	99–100	50	47.8±0.9	94–97

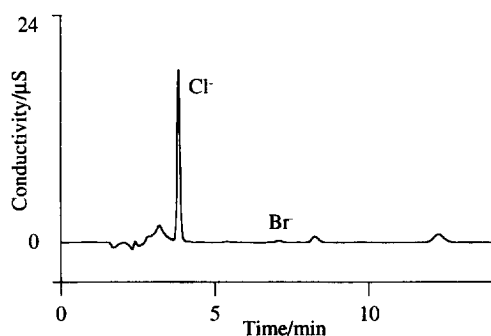


Fig. 3. Chromatogram of GSJ reference material, JB-2, spiked with 200 µg of chloride and 20 µg of bromide (suppressed conductivity detection).

other hand, is carried out at lower temperatures, approximately 650–700°C, in order to extract the halogens as halide ions which are then leached from the fusion cake. The agreement between these two methods for chlorine is very good, with the regression given below.

$$y = 1.006x + 22.619 \quad r^2 = 0.9984 \quad (1)$$

The chlorine data for a selection of rock types using fusion, pyrohydrolysis and aqueous leaching are summarised in Table 3.

Similar data for bromine are summarised in Table 4. Very few bromine data are available as the majority of the samples were below the detection limit of each method, showing that naturally occur-

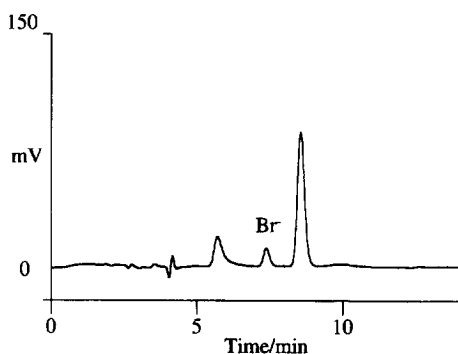


Fig. 4. Chromatogram of GSJ reference material, JB-2, spiked with 200 µg of chloride and 20 µg of bromide (UV detection at 210 nm with f.s.d. at 1 V).

Table 3

Comparison of the chlorine data obtained by the three different methods

Sample	Fusion (mg/kg)	Pyrohydrolysis (mg/kg)	Aqueous leach (mg/kg)
Sandstone	265±22	301±18	228±9
Breccia	130±16	114±24	96±3
Volcanic	144±9	135±16	101±8
Volcanic	58±2	44±11	40±1
Breccia	614±31	602±27	637±18
Limestone	140±31	81±16	85±8
Volcanic	1326±28	1201±23	1095±165
Sandstone	3860±70	3845±33	4021±240

ring concentrations of bromine in rocks are often below 1 mg kg⁻¹. The different detection limits between methods is because of the varying sample weight–volume ratios used and any further analytical dilutions applied.

The relative standard deviation for chlorine in these rock types, based on overall errors incorporating duplicate fusions and solution pre-treatment and duplicate and replicate analysis, is better than 12% for all samples, except for the carboniferous limestone (at 22.5%).

3.5. Limits of detection

The limit of detection for chlorine, based on three standard deviations of the blank, is 36 mg kg⁻¹ and that for bromine, based on the smallest quantifiable bromide peak, is 3 mg kg⁻¹.

Table 4

Comparison of the bromine data obtained by the three different methods

Sample	Fusion (mg/kg)	Pyrohydrolysis (mg/kg)	Aqueous leach (mg/kg)
Sandstone	<3	<6	<0.6
Breccia	<3	<6	<0.6
Volcanic	<3	<6	<0.6
Volcanic	<3	<6	<0.6
Breccia	<3	<6	<0.3
Limestone	<3	<6	1.3±0.2
Volcanic	<3	<6	1.3±0.3
Sandstone	4.5±0.9	<6	3.7±0.3

4. Conclusions

All stages of the method involving alkaline fusion, sample pre-treatment and analysis are relatively simple, inexpensive and rapid, using readily available chemicals and equipment. The use of ion chromatography detection allows the simultaneous detection of chlorine and bromine, in contrast to colorimetry or ion-selective electrodes. The method gives good agreement with chlorine values in reference materials and reasonably accurate and precise spike recoveries for both chlorine and bromine. The chlorine data obtained for the set of test rock samples shows good agreement with data obtained by pyrohydrolysis with colorimetric detection, with no significant methodological bias being evident. There is also reasonable agreement between the data obtained by fusion and the leachate data, indicating that aqueous-leachable chlorine is dominant in most of the samples tested. However, in some cases, non-aqueous-leachable chlorine in the rock matrix comprises a significant fraction of the whole rock analysis, suggesting that the alkaline fusion method is successfully accessing total chlorine. Very few positive data were obtained for bromine. However, of the seventeen reference materials listed in Imai et al. [10] only seven had data for bromine; of these five had only one contributing analysis. This illustrates the practical problems of detecting bromine in rocks. The fusion method appears to be as good as existing methods, although for practical purposes an

improvement in the bromine detection limit of at least one order of magnitude would be desirable.

Acknowledgments

The authors would like to thank Ms. J.M. Cook for her constructive comments on the manuscript. This paper is published by permission of the Director of the British Geological Survey (Natural Environment Research Council).

References

- [1] H.R. Von Gunten, A. Wyttenbach and W. Scherle, *Geochim. Cosmochim. Acta*, 29 (1965) 475.
- [2] N.W. Bower, E.S. Gladney, R.C. Hagen and P.E. Trujillo, *Geostand. Newsl.*, 9 (1985) 199.
- [3] B. Schnetger and Y. Muramatsu, *Analyst*, 121 (1996) 1627.
- [4] Y. Takaku, T. Shimamura, K. Masuda and Y. Igarashi, *Anal. Sci.*, 11 (1995) 823.
- [5] H.N. Elsheimer, *Geostand. Newsl.*, 11 (1987) 115.
- [6] J.M. Cook and D.L. Miles, *Institute of Geological Sciences Report 80/5*, 1980.
- [7] K.G. Heumann, M. Gall and H. Weiss, *Geochim. Cosmochim. Acta*, 51 (1987) 2541.
- [8] D. Whitehead and J.E. Thomas, *Anal. Chem.*, 57 (1985) 2421.
- [9] D.M. Zall, D. Fisher and M.Q. Garner, *Anal. Chem.*, 28 (1956) 1665.
- [10] N. Imai, S. Terashima, S. Itoh and A. Ando, *Geostand. Newsl.*, 19 (1995) 135.