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Trace Analysis of Halogens by Neutron Activation

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Table 1.   Specific rate constant at various concentrations and temperature

Cell conc. in moles of 2,4-dinitrochloro-benzene	k (liter mole⁻¹ minute⁻¹)		
	0.2°C	25°C	40°C
.0010	0.3263	1.603	4.127
.0020	0.3212	1.834	4.526
.0025	0.3238	1.797	4.909
Cell B			
.0010	0.3229	1.650	4.195
.0020	0.3064	1.754	4.094
.0025	0.3122	1.825	4.732

The change in entropy of the system was -21.84 cal. deg.$^{-1}$ mole^{-1}.

Literature Cited

1. J. F. Bunnett and H. D. Crockford. *J. Chem. Ed.* 33, 556 (1956).
2. *Ibid.* p. 553.

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Abstract. A procedure was developed by which trace quantities of chlorine, bromine, iodine, tellurium, and uranium could be quantitatively determined simultaneously in a single meteorite sample. Meteoritic material was irradiated with thermal neutrons. Carrier ions were added, the material was fused with sodium peroxide and the chlorine, bromine, and iodine were isolated. Distillation from a sulfuric acid solution removed the halogens from the bulk of material. After distillation, selective solvent extractions were used to separate and purify each of the halogens. The purified halides were precipitated as the silver halides, weighed, mounted, and counted by β, γ, and/or β-γ coincidence counting techniques.

INTRODUCTION

The problem of analysis of halogens in meteorites is characterized by the unique nature of the matrix and the trace concentrations of halogens present. The difficulty of conventional wet analysis of such samples has contributed to a lack of reliable data for halogen content of meteorites and rocks. Extreme care is necessary to avoid loss of volatile halides during

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[1] The actual experimental work was done at Argonne National Laboratory while the author was participating in the ACM-Argonne Semester Program and the ANL Student Research Aide Program.

dissolution of sample and to prevent halide contamination from reagents or other sources.

Recently Reed (1) successfully used an activation procedure to determine the fluorine content of chondritic meteorites. The complete halogen content of the same or similar samples was of interest. Activation analysis provides important advantages as an analytical method in this case. It is highly sensitive and is free from most of the possibilities for contamination errors.

Many of the elements in a meteorite undergo an (n, γ) re-action with the formation of the corresponding radioisotopes when irradiated with thermal neutrons. The amount of the radioisotope formed is proportional to the amount of the particular element, the neutron flux, and the reaction cross section. The particular reactions of interest are listed in Table 1.

Table 1. n, γ Reactions

Naturally Occuring Stable Isotope	Abundance %	Isotopic Cross-Section Barns	Isotope Formed	Half Life	Method of Decay	Isotope Formed
Cl^{35}	75.4	4.3	Cl^{36}	$4 \times 10^5 y$	β^-	Ar^{36}(stable)
Cl^{37}	24.6	0.6	Cl^{38}	37.3m	β^-,γ	Ar^{38}(stable)
Br^{79}	50.6	2.6	Br^{80m}	4.6hr	IT,γ	Br^{80}
		7.6	Br^{80}	18m	β^-,β^+,K,γ	Kr^{80}(stable)
Br^{81}	49.4	2.6	Br^{82}	35.9hr	β^-,γ	Kr^{82}(stable)
I^{127}	100	6.1	I^{128}	25m	β^-,γ	Xe^{128}(stable
Te^{130}			Te^{131}			I^{131}

The activity of chlorine-38 can be used as a measure of the amount of chlorine present, while the combined activity of the bromine-80m and bromine-82 isotopes can be used to determine the bromine content. Iodine is measured by determining the activity of the iodine-128 isotpe. But the activated iodine re-moved from the sample also contained the isotopes, iodine-131 to iodine-135. Iodine-131 is produced in the decay of tellurium-131 which is produced by the (n, γ) reaction of tellurium-130. Other iodine radioisotopes are produced in the fission of uran-ium-235. Thus selective counting techniques must be used so that the tellurium and uranium abundances can be determined along with the three halogens.

EXPERIMENTAL

Samples and Monitors

The samples were prepared by carefully crushing meteoritic material and placing 0.5 to 1 gm in a polystyrene vial with a

tightly fitting polyethylene cover. Two types of monitors were used. The bromine monitor was prepared by stippling the ammonium salt onto a small clean piece of 10-mil polyethylene and enclosed by heat-sealing it to another piece of polyethylene. Activity of the irradiated polyethylene was discriminated by β - γ coincidence counting. A second type of monitor was used for Cl, I, Te, and U determinations. Known amounts of the ammonium halides, or the nitrates of tellurium and uranium, were stippled onto separate filter paper discs and dried. Following their irradiation, the discs were placed into a solution containing the appropriate carrier and purified in a manner analogous to the samples.

Irradiation

Samples and monitors were irradiated for one-half hour at a flux of ~5 X 10^{12} neutrons per sq. cm. per second in the isotope tray (where the epi thermal neutrons were at a minimum) of the CP-5 reactor at Argonne National Laboratory. Longer periods of irradiation would give greater sensitivity, but these conditions were adequate for this work.

Chemical Separations

For some samples, the amount of desired element in soluble form and the amount in insoluble form was determined. The irradiated sample was placed into water (or other solvent in which one was determining the leachability) which contained known amounts of carrier ions for each of the elements. After the desired leaching time, the sample was removed by centrifugation, washed, and dried. The leach solution was oxidized with ~2 gms of Na_2O_2.

After being dried, the sample was placed into a Ni crucible along with 1 gm of Na_2CO_3 on which carrier ion solutions had been dried. Another gram of Na_2CO_3 two grams NaOH, and five grams of Na_2O_2 were added and the mixture was fused for 10 minutes. The fusion cake was dissolved in water. Both the fusion and leach solutions were reduced with a slight excess of hydroxylamine sulfate. At this point both solutions were at virtually the same state and were processed subsequently in the same manner.

About 15 ml of conc. H_2SO_4 was added to the solution in a distilling flask. After adding a few drops of $NaNO_2$ the iodine evolved as I_2 with only a small amount of heating. The I_2 was collected in a flask containing aqueous NaOH and CCl_4. This solution was set aside and the distillation was continued with a new receiver until the HCl and HBr had been collected in a NaOH solution.

The iodine-containing solution was placed in a separatory funnel and acidified with HNO_3. Upon addition of $NaNO_2$, the funnel was shaken for a few minutes to extract I_2 into the CCl_4. The organic phase was separated, and the aqueous phase was extracted with two or three more fresh 20 ml portions of CCl_4. The aqueous solution was added to the solution containing HBr and HCl evolved from the sample in initial treatment. The iodine extraction process was repeated on this solution to insure removal of iodine that may not have been collected in the first part of the sample distillation. The organic extracts were combined and shaken with 50 ml of water containing NaOH until the CCl_4 became colorless. The aqueous phase was placed in a clean separatory funnel with hold-back carriers for bromine and chlorine, and the iodine was re-extracted as I_2 into CCl_4 following treatment with $NaNO_2$. This cycle of purification was carried out a total of two or three times. Between each cycle an iron hydroxide scavenging step was inserted. After the final extraction into the aqueous phase, several ml of 1% sodium hydrogen sulfite was added, the solution was acidified with HNO_3, and the iodine was precipitated as AgI with O.1N $AgNO_3$. The chemical yields were between 80-90%.

In the meantime, iodine hold-back carrier was added to the aqueous solution containing the chloride and bromide. The hold-back iodide was extracted as before and discarded. Then 20 ml of fresh CCl_4 was added. 1N $KMnO_4$ was added dropwise to oxidize bromide to Br_2. When a slight excess of $KMnO_4$ was signalled by persistence of purple color, the Br_2 was extracted into the organic layer which was separated and removed. Following two or three repeated extractions, the organic extracts were combined. The bromine was stripped from the CCl_4 with water and enough $NaHSO_3$ to decolorize the CCl_4. The aqueous phase was placed in a beaker, acidified with HNO_3 and warmed to destroy SO_3^{2-}. Iodine and chloride hold-backs were added, the iodide was extracted and discarded and the bromine was separated as before. The cycle was repeated one more time using two iron hydroxide scavenging steps. Silver bromide was precipitated from the acidic solution by adding O.1N $AgNO_3$. The chemical yields were usually between 50-60%.

After the iodine and bromine were extracted, the remaining solution was placed in a flask with 15 ml of conc. H_2SO_4 and redistilled into NaOH solution. (The first few ml of the distillate were discarded.) The distillate was placed in a separatory funnel with iodide and bromide hold-back carriers which were extracted, as before. After a iron hydroxide scavenging step, the solution was acidified with HNO_3, and the chloride was precipitated as AgCl. As a final purification step, the precipitate

was dissolved in NH_4OH and another iron hydroxide scavenging step was used. The solution was again acidified giving AgCl. The chemical yields were 60-70%.

The monitors were processed in a similar manner, but they required less purification (however, the uranium- and tellurium-generic iodine monitors required more purification).

The silver halide samples were isolated on pre-weighed filter paper discs in a filter chimney. They were washed with water, alcohol, and ether, and then dried. The discs were weighed, then mounted on stainless steel planchets and covered with a small piece of a sheet of poly-vinyl plastic (or similar material).

Determination of Activity

The decay schemes of the desired elements permitted different counting methods. In most cases a gas-flow type proportional counter was used to count the iodide and bromide. In some cases the ४ spectrum was examined, and in others, B - ४ coincidence counting was used as a check. The long-lived iodine (daughter of tellurium and uranium) and the bromine were counted in the β- ४ coincidence made, which was a 3 x 3 inch NaI (Te) crystal detector and a gas-flow β - proportional counter coupled so that only β - ४ coincidences were registered.

RESULTS AND DISCUSSION

Table 2 gives some typical results using this method to indicate the sensitivity of the method. The uncertainty is due mainly to counting statistics. The method is capable of higher sensitivity than indicated if less time is taken in the purification steps.

In all cases, precautions were observed to obtain radio-chemically pure precipitates. In most cases the purity was confirmed in several manners. 1) The gamma spectrum and β-absorption characteristics were examined, and they indicated only the proper energies. 2) The decays were followed to establish the half lives. In most cases the decays were good after the tail of longer-lived components was subtracted. 3) The results were confirmed by the fact that different counting techniques (β, ४ , and β- ४ coincidence) gave the same results.

The method apparently gives complete isotopic exchange in accordance with the suggestion of Kleinberg and Cowan[2] that strong oxidation followed by reduction was sufficient to give exchange. Known amounts of Cl, Br, and I were run as a check for the monitors and the chemical procedure. The results established the accuracy of the procedure. In another interesting experiment a small amount of the mineral apatite was dug out of an iron meteorite and the chlorine content determined by this method. According to electron microprobe data, the min-

Table 2   Representative Abundances of Halogens, Tellurium and Uranium in Chondritic Meteorites by Neutron Activation

Abundances given in grams of element per gram of meteorite

Meteorite	Cl 10^{-6} grams	Br 10^{-7} grams	I 10^{-8} grams	Te 10^{-6} grams	U 10^{-8} grams
HYPERSTHENE					
Bruderheim	50.0 ± 2	$0.52\pm.07$	$\leqslant5.3$	$0.31\pm.01$	1.75
Harleton	80.0 ± 3	$1.3\pm.1$	$5.4\pm.8$	$0.43\pm.01$	$.95$
New Concord	31.0 ± 1	$.79\pm.06$			
BRONZITE					
Allegan	$7.9\pm.1$	$1.4\pm.2$	$6.9\pm.4$	$0.40\pm.01$	1.1
PIGEONITE					
Lance	125 ± 3	26 ± 3	11 ± 1	$1.01\pm.04$	$.7$
Karoonda	117 ± 3	15 ± 2	22 ± 1	$1.46\pm.05$	
ENSTATITE					
Abee	432 ± 10	35 ± 5	$\leqslant18$	$2.75\pm.06$	
Hvittis	328 ± 11	15 ± 1	9.9 ± 2.5	$0.20\pm.01$	$.14$
Indarch	580 ± 30	65 ± 3	47 ± 5	$2.52\pm.05$	1.5
CARBONACEOUS					
Orgueil	210 ± 10	20 ± 1	23 ± 9	$1.04\pm.06$	$>.6$
Ivuna	240 ± 4	110 ± 10	121 ± 3	$5.77\pm.55$	$.7$

eral (which was partly chlorapatite) should have contained 3% Cl by weight. Within the limits of weighing the original sample, this method confirmed the value of 3% Cl in apatite.

This procedure worked excellently for the analysis of meteorites and with little or no change can be adapted for the analysis of rocks.

Literature Cited

1. G. W. Reed, *Geochim. et Cosmochim. Acta,* 28, 1729 (1964)
2. J. Kleinberg and G. A. Cowan, *The Radiochemistry of Fluorine, Chlorine, Bromine and Iodine.* (NAS-NS 3005), National Academy of Sciences, Washington, D. C., 1960.