Determination of Chlorine in Rocks, Soils and Organic Materials by Heating Powdered Sample in Strong Phosphoric Acid, and Some Additional Investigations on the Related Reactions

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The decomposition of several salts in strong phosphoric acid (SPA) was examined. These halides were decomposed and hydrogen halides evolved by heating the samples with SPA at various temperatures. Based on these data an adequate reagent was chosen for the efficient separation of various elements which can form volatile halides. The recommended distillation condition was applied to determine the chlorine content in solid samples, such as rocks, soils or some organic materials. The sample was heated in an SPA medium and a distillate of hydrogen chloride was absorbed in a sodium hydroxide solution. The solution was subjected to volumetric analysis with a silver nitrate solution for chlorine in the range of 10^{-2} to 10^{-4} mol and to spectrophotometric determination with mercury thiocyanate for elements less than 10^{-4} mol. Furthermore, from the results of X-ray diffraction measurements of the original and the SPA-treated samples, it was confirmed that the main crystal structure of a rock sample could be decomposed by heating with SPA. The chlorine analysis was performed for Japan Geological Survey standard rocks, JG-1 and JB-1, and a synthesized complex compound.

It is known that some metallic and ammonium salts of acids of low boiling point could readily be decomposed in strong phosphoric acid by heating and evolve gaseous acid quantitatively.[1] Sulfides and halides fall in this category, and, based on this various applications have been developed for the determination of sulfur.[2-12]

On the other hand, when an element having a volatile halide is present in a sample, an exchange reaction may occur in the strong phosphoric acid medium, if the sample is heated together with the alkali halide in the medium. In the previous papers,[13,14] the present authors reported that when selenium-containing samples of rocks, soils, or sediments are heated with ammonium chloride or ammonium bromide in SPA, selenium(IV) tetrachloride or tetrabromide, respectively, evolve quantitatively from the sample.

The decomposition of metal halides and the evolution of hydrogen halide may be expressed as

$$X^- + H_nP_mO_l \longrightarrow HX + H_{n-1}P_mO_l^- \qquad (1)$$

and the succeeding reaction with selenium(IV) and (VI) compounds is

$$H_2SeO_3 + 4HX \longrightarrow SeX_4 + 3H_2O \qquad (2)$$

In Eq. 1, the evolved hydrogen halide may be in an extremely reactive gaseous state. To accomplish the two reactions successfully for the quantitative recovery of selenium from a sample, Reaction 1 should proceed concurrently with Reaction 2; Therefore, the forming rate of the active hydrogen halide upon heating of the SPA medium may be the first important practical factor, and the boiling temperature of the selenium halide and the rate of Reaction 2 may be the second.

The present authors investigated the above factors in detail with the aim of extending the SPA-analytical method to the determination of halogens in solid samples such as rocks, soils, and organic materials and to the rapid separation of selenium and arsenic[15] as halides in solid samples.

Experimental

Reagents. *Strong Phosphoric Acid (SPA)*: Commercial ortho-phosphoric acid of extra pure reagent grade was dehydrated as described previously.[13,16] The syrupy liquid obtained was stored in a closed vessel.

Silver Nitrate Standard Solution (M/10). *Mercury Thiocyanate Solution*: Mercury(II) nitrate (5 g) was dissolved in 200 ml of 0.5 M nitric acid; 3 ml of a saturated ammonium iron(III) sulfate solution in 1 M nitric acid was added; the solution was titrated with a 4% potassium thiocyanate solution with continuous shaking until the color changed to pale orange; the white crystalline precipitate thus obtained was filtered through a glass filter, washed well with distilled water and dried in air; 0.3 g of this reagent was dissolved in 100 ml of ethanol and stored in a dark bottle. This solution is stable for several months.

Ammonium Iron(III) Sulfate Solution: Six grams of dodecahydrated salt of guaranteed reagent grade was dissolved in 100 ml of 6 M nitric acid.

Standard Chloride Solution: Sodium chloride of guaranteed reagent grade (2.013 g) was dissolved in distilled water in a 1-liter measuring flask. This solution was diluted for use.

Other Chemicals: Ammonium chloride, bromide, and iodide, potassium chloride, bromide, and iodide, sodium chloride, bromide, and iodide, hydrochloric acid, sodium hydroxide and fluorescein were all of guaranteed reagent grade.

Apparatus. Electric conductivity measurements: a conductivity outfit, Model MY-7 (Yanagimoto Seisakusho Co.) connected to a conductivity cell, Model CDC-121 (M & S Instr. Co., Inc.).

A photo-electric spectrophotometer (Hirama Rika Kenkyujo), Type 6 and 1-cm glass cell.

A Hitachi-Horiba glass electrode pH meter, Model M-3.

The reaction vessel used was the same as that described previously[13] and was connected to an absorption tube or a conductivity cell.

Procedure. Sodium chloride in amounts of 5×10^{-4}—2×10^{-3} mol was placed in the reaction vessel and about 30 g of SPA was added. Twenty milliliters of a sodium hydroxide solution was placed in the absorption tube and all joints were connected as shown in Fig. 1. The air was aspirated slowly from the last outlet tube by means of a suction pump and the reaction vessel was heated on an electric heater to start the reaction. The reaction rate was followed every 2—3 min by measuring the electric conductivity of the absorption solution using a flow-type conductivity cell. The temperature of the reaction medium was recorded at the same time. The evolving hydrogen chloride in the

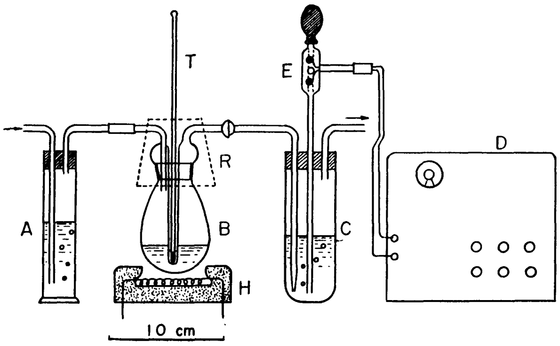


Fig. 1. Apparatus for successive conductivity measurement for SPA-distillate absorbing solution.
A: Washing bottle, B: reaction vessel, C: absorption tube, D: conductivity outfit, E: flow-type conductity cell, H: electric heater, R: ribbon heater, T: thermometer.

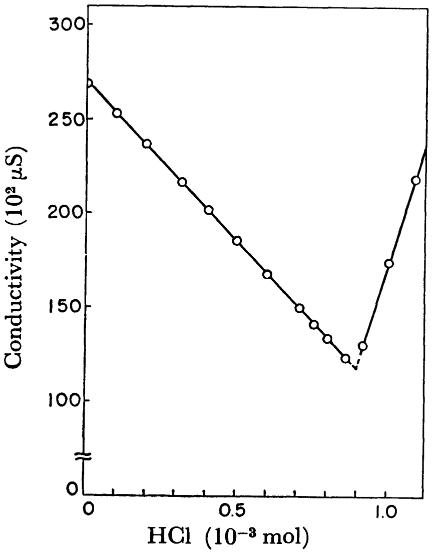


Fig. 2. Conductometric titration curve.
Sodium hydroxide was titrated with hydrochloric acid.

absorption solution was determined from the conductivity value obtained. The relationship between the evolving hydrogen chloride and the electric conductivity was obtained using the titration curve (Fig. 2) which was constructed on the basis of the titration of 20 ml of a M/20 sodium hydroxide solution with 1 M hydrochloric acid. In the case of decomposing bromide or iodide salts, hydrobromic acid or hydroiodic acid were used in place of hydrochloric acid in the above procedure.

Results and Discussion

Decomposition of Various Halide in SPA. Figures 3, 4, and 5 show decomposition curves for several chlorides, bromides and iodides in SPA media. In the figures, the open circles represent the amounts of hydrogen halide trapped in the absorption solution after each heating period as determined by the conductivity measurements and the filled-in circles the temperature of the reaction medium after the same periods. It is clear that the decomposition of chloride salts is initiated at about 110, 50, and 50 °C and the evolution of hydrogen chloride may be completed at 200, 230, and 160 °C, for the sodium, potassium, and ammonium salts, respectively. In the case of the bromides, the sodium salt was most resistant to decomposition, and the ammonium salt reacted with SPA more easily than did the others. For the iodides, again the sodium salt was most resistant to SPA action, whereas the potassium salt was most easily decomposed. The results

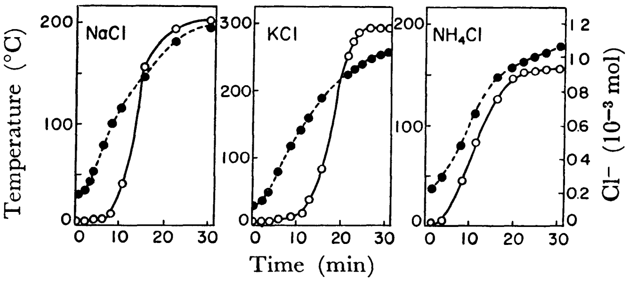


Fig. 3. SPA-decomposition curves for cloride salts.
—O—: Amount of hydrogen chloride in absorption solution, --●--: temperature change of SPA-medium.

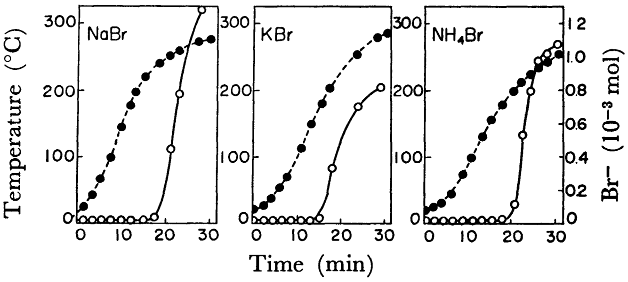


Fig. 4. SPA-decomposition curves for bromide salts.

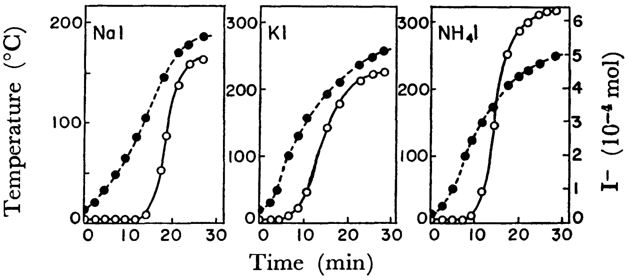


Fig. 5. SPA-decomposition curves for iodide salts.

Table 1. Decomposition temperature of various halide salts in SPA media

Salt	Temperature of decomposition, °C	
	Start	Finish
NaCl	100	200
KCl	50	230
NH_4Cl	50	160
NaBr	230	290
KBr	180	280
NH_4Br	180	260
NaI	180	260
KI	80	230
NH_4I	100	240

are summarized in Table 1. However, it should be noted that there is a certain time lag between the hydrogen halide generation and its arrival in the absorption solution. Furthermore, the present results may fluctuate to some extent depending on the heating time and also on the amounts of halide salts used. The difficulty in detecting halide ions in amounts less than 2×10^{-5} mol in 20 ml of the absorption solution makes it necessary to delay the measurement until the evolved hydrogen halide gas has accumulated in detectable amounts in the solution. Therefore, a delay is unavoidable in the response of the hydrogen halide gas evolution and the completion of the decomposing reaction. Therefore, the data shown in Figs. 3, 4, and 5 are strictly valid only under the present experimental conditions.

But it may be possible to present a discussion based on the present results which may be not differ too much from those obtained for arbitrary experimental conditions. As suggested above, a complete distillation of a certain element in gaseous halide form from the SPA medium would be expected to occur when decomposition of the halide reagent added to the sample in the reaction vessel begins as the increasing temperature approaches the boiling point of the halide of the element concerned and ceases at temperatures above the boiling point. Thus, from the present results it may be possible to predict which reagent is suitable for use in the distillation of a given element by evolution as a gaseous halide from an SPA medium.

Distillation of Selenium and Arsenic as Halides. As previously reported,13) selenium(IV) and (VI) can be distilled as tetrabromide from bromide–SPA at about 250 °C. The sublimation temperature of the selenium tetrabromide is known to be 196 °C. Therefore, sodium chloride and ammonium chloride are presumed to be unsuitable for the distillation of selenium since hydrogen chloride gas will evaporate off before the temperature reaches the sublimation point of selenium tetrachloride. In fact, ammonium and sodium chlorides distill selenium incompletely (50—80%).

On the other hand, ammonium bromide was found to be the most useful for this purpose, although the sublimation temperature of selenium(IV) tetrabromide is still unknown. This temperature may fall between 200 and 250 °C, because the boiling point of a metal bromide in an aqueous solution is generally higher than that of the corresponding chloride.

For arsenic(III), the boiling point of arsenic(III) chloride and bromide are known to be 130.4 and 221 °C, respectively.17) Thus the chloride would be expected to be the most adequate form for distillation from the SPA medium. Therefore, sodium and potassium chlorides may be useful for this purpose. As shown in Fig. 6, the distillation of arsenic(III) was complete in the sodium chloride–SPA reagent solution when the temperature reached 180 °C and a slightly lower recovery was observed when potassium chloride was used.15) On the other hand, the recovery of arsenic by ammonium bromide was incomplete as expected.

Another example is the distillation of germanium. The boiling points of germanium(IV) chloride and bromide are known to be 84 and 185.9 °C, respectively.17) Therefore, ammonium or potassium chloride may be suitably employed for the distillation of germanium in tetrachloride form, whereas all bromides are useless. Tin(IV) can also be distilled as tin(IV) chloride (bp 114 °C) or bromide (bp 202 °C) from ammonium chloride–SPA and ammonium bromide–SPA media.

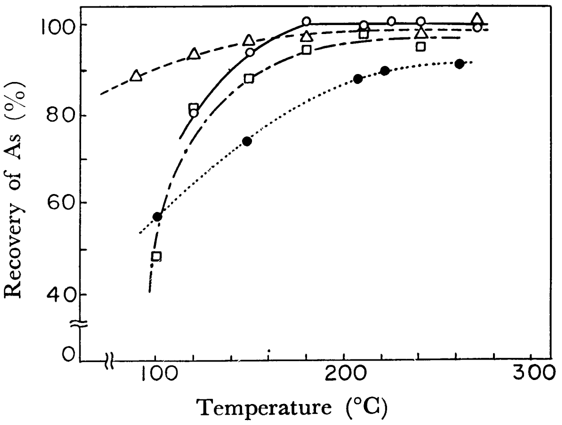


Fig. 6. Recovery of arsenic at various temperatures of various SPA-reagents media.
—○—: NaCl, --△--: KCl, —□—: NH_4Cl, ···●···: NH_4Br.

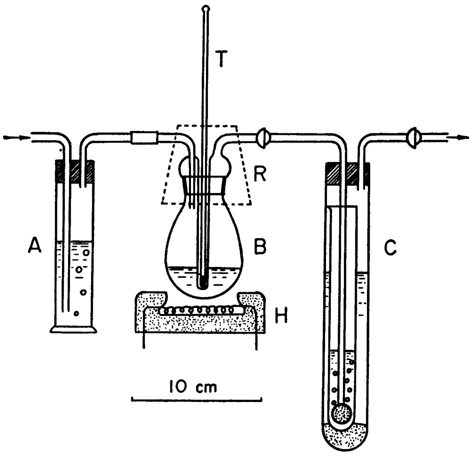


Fig. 7. SPA distillation apparatus for determination of halogen.
A: Washing bottle, B: reaction vessel, C: absorption tube, H: electric heater, R: ribbon heater, T: thermometer.

Further predictions will be made for the distillation of the other volatile metal halides, for example, chromium, niobium, rhenium, and antimony.18) Further details and applications of the present study will be given elsewhere.

Determination of Chloride in Solid Samples. In general, the analysis of chlorine content in rocks, soils, and minerals requires an alkaline or carbonate fusion treatment of the sample, followed by extraction with hot water or nitric acid. The fusion process is tedious and may cause unexpected losses of the element or contamination of the element from the reagents used and from the instruments. Furthermore, matrix constituents occasionally interfere with the determination

Table 2. Volumetric determination of chloride after SPA distillation

Cl$^-$ added, mol$^{a)}$	Cl$^-$ found, mol
1×10^{-3}	1.01×10^{-3}
	1.00
	1.02
	1.00
1×10^{-4}	1.01×10^{-4}
	0.98
	1.02
	0.99
	0.98

a) Cl$^-$ was added as NaCl.

Table 3. Spectrophotometric determination of chloride after SPA distillation

Cl$^-$ added, mol$^{a)}$	Cl$^-$ found, mol
3.4×10^{-5}	3.2×10^{-5}
	3.1
	3.5
	3.3
5.0×10^{-6}	4.8×10^{-6}
	4.7
	5.2
	4.9

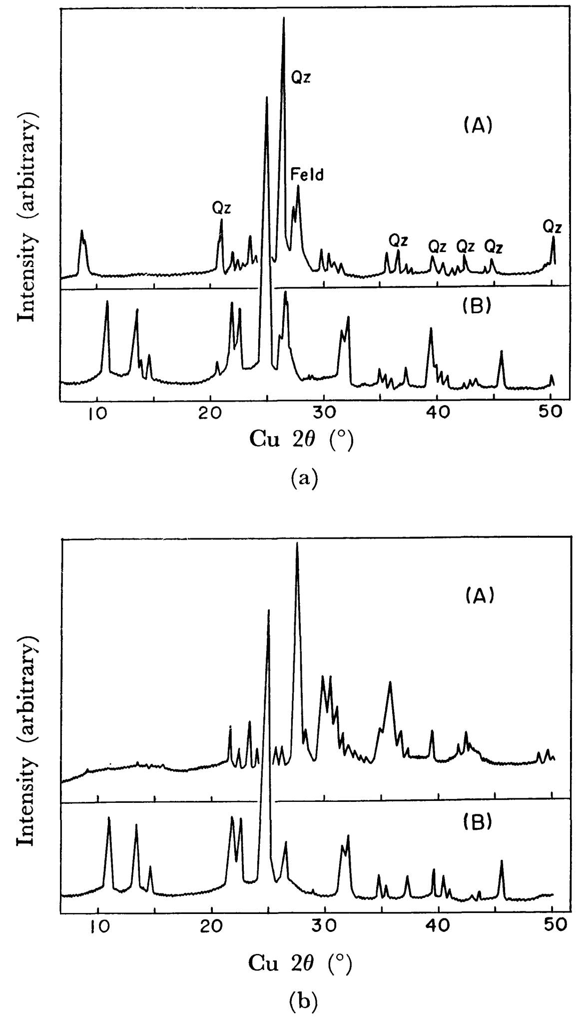
a) Cl$^-$ was added as NaCl.

of chloride in low concentrations. Thus, it is desirable to separate chlorine from the matrix more rapidly and effectively.

As mentioned above, many chloride compounds were quantitatively decomposed and chloride was distilled off as hydrogen chloride from SPA media by heating to about 250 °C. Therefore, the present method seems to be applicable to the determination of chlorine in chloride or other halide form in solid materials, such as rocks, minerals, soils, biological materials, and complex compounds.

The apparatus used is shown in Fig. 7. The procedure is as follows. A suitable amount of the sample (0.5—1.0 g) was placed in the reaction vessel (B), and about 30 g of SPA was added. An accurately-determined amount of 20 ml of a 0.05 M sodium hydroxide solution was put into the absorption tube (C), which was placed in a wider test tube containing cooling water. Then all joints were connected as shown in the figure. (A) is a gas-washing bottle containing a 0.1 M silver nitrate solution. Air was aspirated slowly from the last outlet tube and the reaction vessel was heated with an electric heater until the temperature of the contents reached about 250 °C. Around the cap of the reaction vessel was wound a ribbon heater to avoid trapping of hydrogen chloride at this point during distillation.

After distillation, the absorption and the washing solutions were combined and subjected to chloride measurement. For chlorides in the range of 10^{-3} to 10^{-4} mol, titration was performed with a silver nitrate standard solution using fluorescein as an indicator.



(a)

(b)

Fig. 8. X-Ray diffraction pattern for standard rocks and SPA treated standard rocks.
a: JG-1, b: JB-1.
A: Original rock sample, B: SPA treated rock sample.

For chlorides less than 10^{-4} mol, the determination was made spectrophotometrically using mercury thiocyanate[19] as follows: after distillation, 4 ml of an ammonium iron(III) sulfate solution and 2 ml of a mercury thiocyanate solution were added to the absorption solution. This solution was mixed well by shaking, and then the absorption was measured at a wavelength of 460 nm. In this case, the volume of the absorption solution during distillation appeared to remain unchanged. From Tables 2 and 3, which indicate the results it is clear that the determination of chlorides in the concentration range of 10^{-6}—10^{-2} mol can be performed very satisfactorily.

Decomposition of Rock Samples in SPA Media. When organic compounds or complex materials, such as complex compounds, hair, or rice, are heated in an SPA medium with decomposition of the materials to carbon, chlorine can be evolved as hydrogen chloride. However, a problem remained as to whether or not rock samples could be decomposed. Therefore, in the present study, experiments were carried out to clarify this problem.

Japan Geological Survey standard rocks, JG-1 and

TABLE 4. CHLORINE CONTENTS OF STANDARD ROCKS, JG-1 AND JB-1

JG-1, ppm	JB-1, ppm	Reference
53	178	
57	160	
50	168	
58	175	
52	164	Present results
av 54±4	169±10	
200	—	Sen Gupta (1971)
57	190	Akaiwa *et al.* (1973)
67(5)	167(5)	Terashima (1974)

TABLE 5. DETERMINATION OF CHLORINE IN *trans*-$[CoCl_2en_2]H_5O_2Cl_2$ AFTER SPA DISTILLATION

Sample taken, mg[a)]	Cl, mg	
	Found	Calcd
100.9	38.4	38.7
99.5	38.1	38.3
100.4	38.3	38.5

a) The sample was dried at 100 °C for 1 h.

JB-1, were subjected to treatment with SPA and the remaining white residue were washed with distilled water to remove any phosphoric acid. Then, X-ray diffraction patterns of these crystals was examined and compared with the X-ray diffraction patterns of the original rock samples. The X-ray patterns obtained are shown in Fig. 8. The peaks due to quartz and feldspar in the original JG-1 sample completely disappeared after the treatment, and new peaks appeared. Also, in the case of JB-1, entirely different patterns were observed for the original and the SPA-treated samples. These new X-ray patterns were assigned to $Si_3(PO_4)_4$. From the results, it can be confirmed that the original crystalline structure of silicate minerals in a rock sample is decomposed and then converted into a new crystalline structure whose composition includes SPA and silica. Therefore, it is reasonable to conclude that chlorine can also be completely liberated from a rock sample during decomposition due to heating of the sample in SPA.

In Table 4, the analytical results obtained by the present method for the standard rocks, JG-1 and JB-1, are compared with those reported by Sen Gupta,[20)] Akaiwa[21)] and Terashima.[22)] The present results are in good agreement with those of Akaiwa andTerashima. The value reported by Sen Gupta appears to be too high.

A determination was also carried out for a synthesized complex compound, the structure of which was reported to be $[CoCl_2en_2]H_5O_2Cl_2$.[23)] The data are shown in Table 5. The observed chlorine content coincides fairly well with the calculated result.

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