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DETERMINATION OF CHLORINE IN GRAPHITE
BY COMBUSTION-ION CHROMATOGRAPHY

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Determination of Chlorine in Graphite by Combustion-ion
Chromatography

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A combustion/ion chromatographic method has been studied for the sensitive determination of chlorine in graphite. A graphite sample was burnt at 900°C in a silica reaction tube at an oxygen flow rate of 200 ml/min. Chlorine evolved was absorbed in 20 ml of a 0.1 mM sodium carbonate solution. The solution was evaporated to dryness. The residue was dissolved with a small volume of water. Chlorine in the solution was determined using ion chromatography. The method was applied to JAERI graphite certified reference materials and practical graphite materials. The detection limit was about 0.8 $\mu\text{gCl/g}$ for a 2.0 g sample. The precision was about 2.5% (relative standard deviation) for samples with chlorine content of 70 $\mu\text{g/g}$ level. The method is also usable for coal samples.

Keywords: Chlorine in Graphite, Combustion Method, Ion Chromatography

* China Institute of Atomic Energy

燃焼—イオンクロマトグラフ法による黒鉛中の塩素の定量

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(1995年 8月22日受理)

黒鉛中の塩素の高感度定量法を確立するため、燃焼／イオンクロマトグラフ法に関し検討した。黒鉛試料を石英製ポートにはかり取り、酸素ガスを 200ml/minで通じながら、電气管状炉中で 900℃に60分間加熱して燃焼した。発生する塩素を0.1mM炭酸ナトリウム溶液20mlに吸収させた後、試料溶液を蒸発、乾固した。残渣を少量の水で溶かし定容とした後、イオンクロマトグラフ法により塩素を測定した。確立した方法をJAERI黒鉛分析用標準試料及び黒鉛実用材に適用した。定量下限は、試料はかり取り量2.0gで塩素含有率 0.8 μ g/gであった。繰り返し精度は、塩素含有率70 μ g/gの試料に対して相対標準偏差で約2.5%であった。本法は、石炭中の塩素の定量にも適用できる。

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1. INTRODUCTION

A sizable amount of graphite materials is used in high temperature gas cooled nuclear reactor due to its excellent physical properties. Among these materials, graphite used as a moderator and reflector material has to be of the highest purity¹⁾. The concentration of some impurity elements is in the order of 1 $\mu\text{g/g}$ or less²⁾. Therefore, an accurate determination of the impurity elements is necessary for selecting graphite materials used as the core and core support structural components. Recently, high-purity graphite certified reference materials (CRMs) have been prepared by the Committee on Chemical Analysis of Nuclear Fuels and Reactor Materials, JAERI. In the development of analytical methods for graphite materials, most of the impurity elements studied were metallic except for boron and sulfur³⁾. Nonmetallic elements such as chlorine etc. were also important. Especially, chlorine yields a long lived radioactive nuclide ^{36}Cl ($t_{1/2}=3.00 \times 10^5\text{y}$) by absorbing neutron, which causes an increase in the activation inventory of the reactor⁴⁾.

A certain combustion technique has been used for many years as an effective separation method for determining halogens in geological samples^{5,6,7,8)}. Measurement methods for chlorine include neutron activation analysis^{9,10,11)}, spectrophotometry^{12,13,14)}, X-ray fluorescence spectrometry¹⁵⁾, ion selective electrode^{7,16)} and ion chromatography (IC)^{17,18)}. the IC technique offers certain advantages over other measuring methods: for example, it is sensitive, quick,

easy to operate and requires only a small sample. A pyrohydrolysis-IC method is studied for the determination of fluorine and/or chlorine in inorganic materials^{5,6,7,8,19,20}). However, none has appeared for graphite analysis. In the present paper, combustion-IC has been studied for the sensitive determination of chlorine regarding graphite materials.

2. EXPERIMENTAL

2.1 Apparatus

Ion Chromatography: The system consists of a Hitachi L-5020 column oven, L-6000 pump, L-3720 conductivity detector and D-6100 data station HPLC manager. An anion guard column and anion separator column #2710 were used to measure the chloride. Standard 0.6 mM phthalic acid monopotassium salt - 5% isopropyl alcohol eluent at a flow rate of 1.0 ml/min with a 20 μ l sample injection loop was used for all measurements.

Combustion apparatus: It consists of a silica reaction tube (30 mm in diameter, 300 mm in length), an electric tube furnace with a temperature controller and a gas flow meter. The apparatus is displayed in Fig. 1.

2.2 Reagents and special solutions

Phthalic acid monopotassium salt, isopropyl alcohol, sodium carbonate and all the other chemicals were of reagent grade. Water was purified using a Millipore Milli-Q Lab after distillation.

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Oxygen: The oxygen was humidified by passing it through a 500-ml vial containing water²³).

10 mM phthalic acid monopotassium salt stock solution: 2.04 g of phthalic acid monopotassium salt was dissolved in 1000 ml of water.

Eluent for IC (0.6 mM phthalic acid monopotassium salt - 5 % isopropyl alcohol): 60 ml of the stock solution and 50 ml of isopropyl alcohol were mixed and diluted to 1000 ml using water.

Standard stock solution (1000 $\mu\text{gCl/ml}$): 1.650 g of sodium chloride was dissolved in 1000 ml of water. Calibration solutions were prepared by diluting the stock solution prior to use.

2.3 Procedure

Flow diagram of analytical procedure is shown in Fig. 2.

(1) Sample combustion

An appropriate amount of the sample was weighed in a silica boat and inserted into the center of silica reaction tube installed in the electric tube furnace. The sample was burned by heating it at 900°C in oxygen stream at 200 ml/min for 60 min. The chlorine that evolved was absorbed in 20 ml of a 0.1 mM sodium carbonate receiving solution. The solution was evaporated to dryness. The residue was dissolved with 2.0 ml of pure water.

(2) Determination of chlorine by IC

The IC was calibrated with a set of chlorine standard solutions; 1.0, 2.5, and 5.0 $\mu\text{g/ml}$. The chlorine concentration of the sample solutions was calculated by the use of linear least-squares

regressions. The slope of the calibration curve, peak areas versus concentration, remaining constant throughout the analysis with a linear correlation coefficient of 0.9996. A typical ion chromatogram of the standard solution and sample solution for JAERI-G6 can be seen in Fig. 3.

3. RESULTS AND DISCUSSION

3.1 Combustion condition

A number of burning parameters were optimized to obtain a complete recovery of chlorine from graphite using 2 g of CRM JAERI G6 with an addition of 50 μg of chlorine in the standard solution. The effect of the oxygen flow rate on the recovery was checked by varying the flow rate from 100 to 400 ml/min, while maintaining the furnace temperature at 900°C with a reaction time of 60 min. The recovery was 96~98% at the flow rate of 100 and 200 ml/min. It was slightly higher than those at 300 and 400 ml/min, which was 91~92%. Therefore, the oxygen flow rate was fixed at 200 ml/min throughout this experiment. Figure 4 shows the effect of heating temperature of the sample regarding recovery. Recovery increased with a rise in temperature and became almost constant above 850°C. At 900°C, it took about 30 min for the complete combustion of 2 g of the graphite sample. For a heating time longer than 45 min, the recovery became almost constant: 94~97%, whereas the shorter heating time less than 30 min resulted in a poor recovery. From the above results, the

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burning conditions of graphite were fixed: the heating temperature of 900°C for 60 min with an oxygen flow rate of 200 ml/min.

The effect of sodium carbonate concentration of the receiving solution regarding chlorine recovery was checked by changing its concentration from 0.1~0.4 mM with a fixed volume of 20 ml, using 1 g of JAERI G5 (chlorine content is 75 μg/g). No significant effect was observed, so that 20 ml of 0.1 mM sodium carbonate was used as the receiving solution.

3.2 Blank and detection limit

A procedural blank was determined by following the entire procedure. A blank value of $1.36 \pm 0.56 \mu\text{g Cl}$ (n=6) was obtained. If the detection limit is defined as three times the standard deviation of the blank, as little as 1.7 μg of chlorine should be detected, which corresponded to 0.8 μg/g of the detection limit for the 2.0 g graphite sample.

3.3 Recovery of chlorine

A set of experiments was made to find out the recovery of chlorine from graphite samples, using 2.0 g of JAERI-G6 with an addition of 20 μg of chlorine in the standard solution. Chlorine was determined by following the proposed procedure. The results are shown in Table 1. The recovery of chlorine obtained was 98% with the RSD of 3.5%.

3.4 Determination of chlorine in graphite CRMs and practical samples

The proposed method was applied to JAERI graphite CRMs and practical graphite materials. The results are summarized in Table 2. Precision was about 2.5% RSD for determination of chlorine at 70 μ g/g level of graphite. It is interesting to know that the chlorine content of high-purity graphite CRM JAERI-G5 was much higher than any other graphite materials determined, although the ash content of CRM JAERI-G5 was less than 10 ppm. Probably, the high chlorine content of JAERI-G5 resulted from the residual chlorine compounds, which were used in the purification of the graphite material¹⁾.

To know if the chlorine in the graphite is evolved as a result of heating it in an inert atmosphere, JAERI G5 was heated at 900°C in a nitrogen stream at 200 ml/min. About 60-70% of chlorine in the sample was found to be evolved. This suggests that graphite materials containing significant amount of chlorine were used in the reactor core, corrosive gaseous compounds such as hydrogen chloride may be evolved during the operation of the reactor. So that, it is important to check the chlorine content of the graphite material before use.

3.5 Application to coal samples

To check the accuracy of the present method, chlorine in the coal CRMs {National Institute of Standards and Technology Standard Reference Material (NIST SRM) 1632b and Australian Standard Certified Reference Material (ASCRM) 013-4} was determined. The results obtained can be seen in Table 3. The mean value of the

present method for SRM 1632b is in good agreement with the value obtained by instrumental neutron activation analysis at NIST. It is noted that coal sample should be first dried and oxidized for 30 min at about 250°C prior to burning at 900°C, because coal is oxidized violently at high temperature in the oxygen atmosphere which could lead to an explosion.

Acknowledgment: The authors are very grateful to Dr. T. Adachi, Head of Analytical Chemistry Laboratory, JAERI, for his helpful discussions regarding the publishing of the present paper.

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Table 1 Recovery of chlorine in sodium chloride

No.	Found, $\mu\text{g Cl}$	Recovered, $\mu\text{g Cl}^{\text{a)}$	Recovery, %
1	22.9	19.4	96.8
2	23.7	20.2	101.0
3	22.9	19.4	97.1
4	24.0	20.5	102.5
5	23.3	19.8	99.0
6	22.0	18.5	92.6
Average	23.1	19.6	98.2
s	0.7	0.7	3.5

20 $\mu\text{g Cl}$ in NaCl is added to 2.0 g of JAERI-G6

a) Procedural blank and Cl content in JAERI-G6 are subtracted from the found

Table 2 Determination of chlorine ($\mu\text{g g}^{-1}$) in CRMs JAERI-G5, -G6 and other graphite samples

Sample No.	JAERI-G5 ^{a)}	JAERI-G6	G1 ^{b)}	IG-11 ^{c)}	PGX ^{c)}
Ash content, ppm	<10	220	<10	<100	1300
1	76.0	1.01	6.43	0.99	1.12
2	77.8	1.31	6.45	1.14	0.99
3	74.9	0.90	6.51	0.56	1.90
4	75.2	1.36	5.57	1.01	0.74
5	70.7	0.92	6.14	1.24	0.93
6	75.8	0.98	5.94	0.91	0.97
Average	75.1	1.08	6.17	0.98	1.11
s	2.4	0.20	0.37	0.23	0.41

a) Sample weight: 2.0 g.

b) High purity graphite material prepared for making standard sample.

c) Practical graphite materials

Table 3 Determination of chlorine in coal CRMs ($\mu\text{gCl/g}$)

No.	NIST SRM 1632b ^{a)}	ASCRM-013-4
1	1201	224
2	1196	214
3	1177	242
4	1240	240
5	1286	239
6	1241	250
Average	1224	235
s	39.8	13.2
RSD ^{b)} , %	3.3	5.6

0.5 g of sample is used for the determinations

a) Cl content obtained by the instrumental neutron activation analysis at NIST is $1260 \mu\text{g/g}$, although not certified.

b) Relative standard deviation.

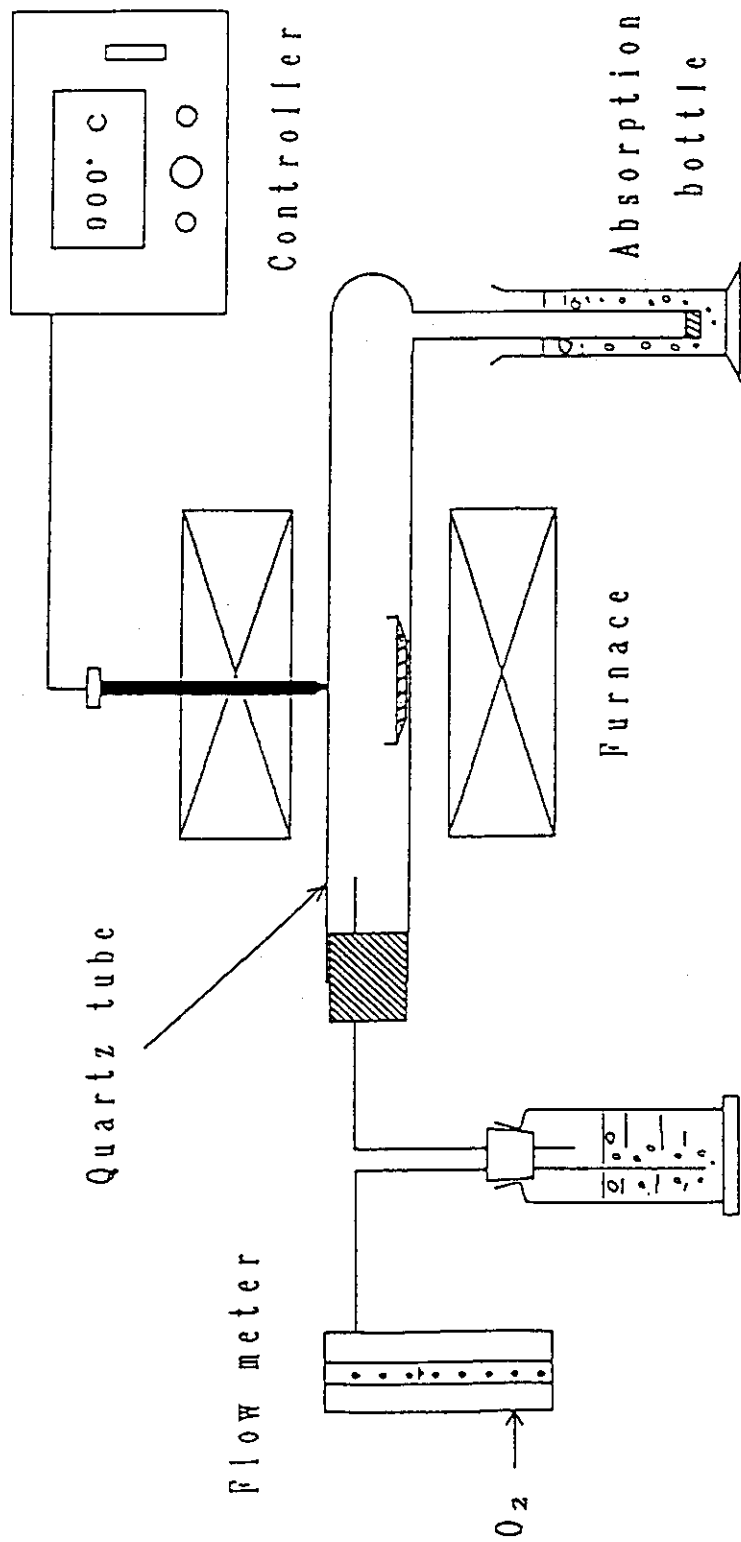


Fig.1 Combustion apparatus

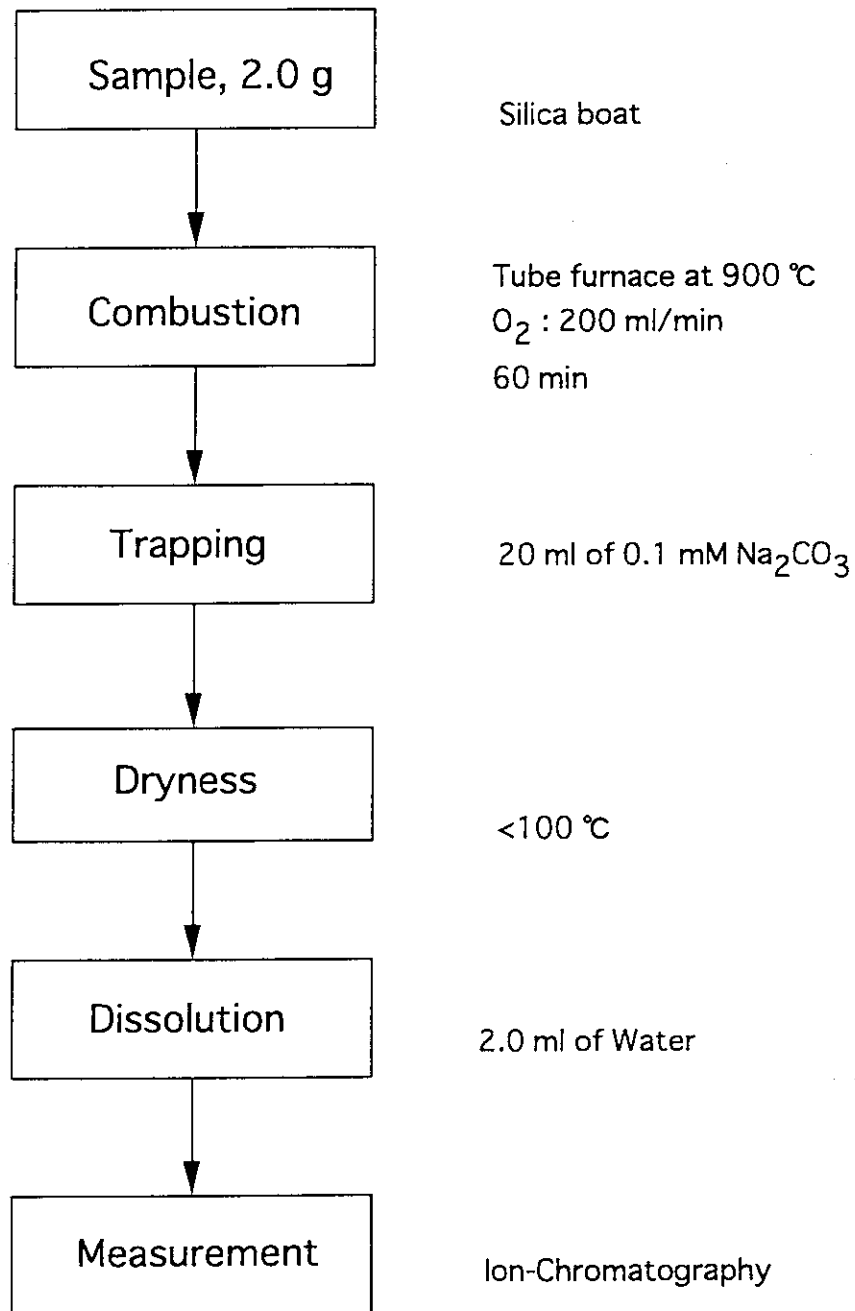


Fig.2 Analytical procedure

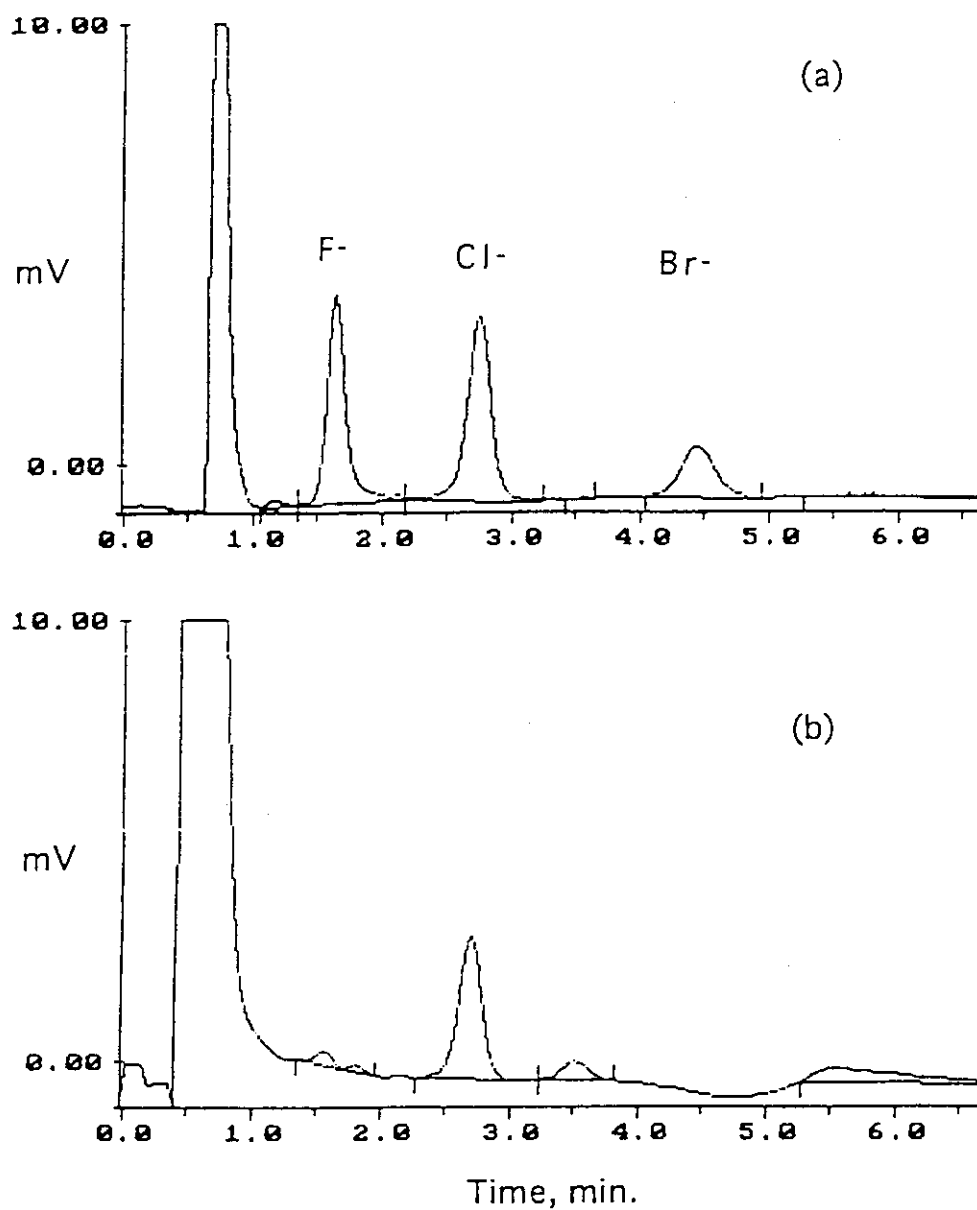


Fig.3 Ion chromatograms of the standard sample solution (a) and the solution obtained by combustion of JAERI-G6 (b)
 (a): standard solution of 2.5 $\mu\text{g/g}$ F, Cl and Br
 (b): 2.0 g of JAERI-G6 is used

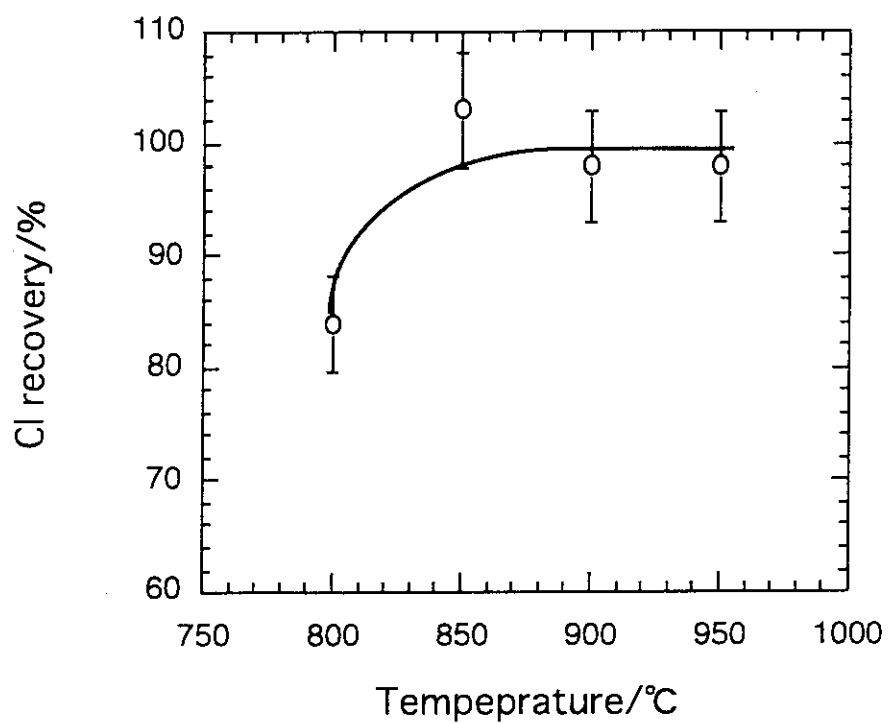


Fig.4 Effect of combustion temperatures regarding chlorine recovery