Determination of Si in Ultra Fine Al₂O₃ Powder Using Matrix Elimination in Inductively Coupled Plasma-Atomic Emission Spectrometry

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It is well known that Al_2O_3 is one of the most important ceramic materials for electronics. The use of it extended over ceramic insulator, and ceramic sensor. Al_2O_3 is also added to ceramic capacitor as a dopant that plays an important role in electronic materials.[1~4] For instance, controlled doping of rare earth oxides in ceramic capacitor material systems results in an n-type semiconductor that shows a resistivity of 10 to 10^4 ohm-cm at room temperature and high positive temperature coefficients of resistance over limited temperature ranges. The resistivity of ceramics made semiconducting by incorporation of conventional dopants is extremely sensitive to the concentration and distribution of dopants, to undesirable impurities and to firing conditions.[1,2] In this matter, the analysis of the basic products is important so as to be able to optimize production procedures, including the exclusion of contamination at the various production stages and tailoring the properties of the material by controlling the levels of impurities.[5]

Generally, most of Al_2O_3 raw material contains some Ca, Mg, Fe, Na, Si, etc., which interfere with semiconduction of ceramic capacitor materials.[4] Deleterious effects of those impurities on the function of electronic products will be crucial. By applying inductively coupled plasma atomic emission spectrometry (ICP-AES), the goal can be reached for the analysis of those undesirable impurities in Al_2O_3 matrix.[5,6,7] It is reported that after careful optimization of the working conditions of ICP-AES, the trace amount of Ca, Mg, Fe, Cu, etc. were determined.[5] However, of the elements existed in Al_2O_3, Si is known to be one of the toilsome elements to be quantitatively determined by ICP-AES because the determination of Si in aluminium matrix has been hampered by difficulty in attaining reasonable reproducibility. In addition, standard ICP torch should be changed into suitable torch because HF solution has to be used to decompose the sample if Al_2O_3 contains more than 1% SiO_2.

Detection of trace elements in aluminium matrix can be improved by applying the complexation method using dithiocarboxylates such as hexamethylenedithiocarbonate (HMDC) to matrix elimination. For instance, adsorption of the HMDC complexes on a reverse phase C_{18} column followed by solid-phase extraction made it possible to remove the matrix.[8] However, this method required high pressure nebulizing system for effluent and cannot apply to the analysis of Si because Si does not form complex with HMDC. For another case of matrix elimination, it was reported that Al can be precipitated under the form of $AlCl_3$ by the addition of an excess of HCl-gas into the sample solution and the supernatant can be delivered into the plasma in order to determine the trace elements in the solution.[5] Although about 99.5% of the Al were precipitated, this method required a special desiccator charged with HCl-gas and more than 48 h in extra besides the sample decomposition time (6 h at 250 ℃).

In this paper the development of atomic spectrometric procedure for the analysis of Si in Al_2O_3 ceramic powder is described. The sample preparation technique, high pressure acid digestion bomb method, studied from previous ICP-AES work in this laboratory[9] is adapted to the sample pretreatment. Specially, a method of matrix removal which leads to the possibility of further improvement of the detection power is investigated by using ion exchange resin. Analytical result of commercially available Al_2O_3 material is presented.

Experimentals

Working procedure for Separation of Si from Al. The sulfuric acid used for the sample decomposition was of Ultrapure grade (Kanto Chemical Co., Japan). All dilution was made with deionized water. All solutions were stored and mixed in especially cleaned polyethylene bottles. Final solutions with matched acid contained 4 μg mL^{-1} of Si in the 8 μg mL^{-1} of Al.

Experiment for the optimization of the separation of Si from Al was carried out. A separation column was prepared by packing 80 mL of Dowex 50W-X4 cation exchange resin into a Teflon column after the resin was generated by soaking in (1+1) H_2SO_4 solution. After 200 mL of the solution containing Si and Al was eluted, the solution was collected and delivered into the ICP to check concentration changes of Si and Al.

For applying this separation method to real Al_2O_3 ceramics, following experiment was performed. Special cleaning and handling precautions are required in order to prevent contamination of samples. About 0.200 g of sample of Al_2O_3 powder was transferred into a Pt crucible (No. 20) followed by addition of 15 mL of (1+3) H_2SO_4. The mixture in the Pt crucible was allowed to react for 40 h at 230 ℃ in high pressure closed poly(tetrafluoroethylene) (PTFE) vessel (model HU-50, Mitsuoshi corp., Nagoya, Japan). The resulting solution was diluted to 200 mL of screw-capped polyethylene volumetric flask, so that final acid volume in the flask was about 1.5%. For more efficient removal of Al matrix, pre-column with 50 mL of Dowex HCR-W2 (50W-X8, 20-50 mesh) cation exchange resin was used before the separation column described above. Stock solution for aluminium matrix was prepared by dissolving 99.999% Al metal with HCl in the presence of cobalt for the enhancement of solubility. Matrix matched standard solutions were prepared by using the spectroscopic standard solutions of 1000 μg mL^{-1}.

Instrumentation. The instrument employed in this study was a Thermo Jarrell Ash (27 MHz, ICAP-757V, USA) ICP-AES operated at 1.0 kW forward power with a coolant flow of 13 *l* $min.^{-1}$, a nebulizer flow of 0.6 *l* $min.^{-1}$, and a sample uptake rate of 2 mL $min.^{-1}$ with a peristaltic pump. To determine the quantities of Al and Si in the solution,
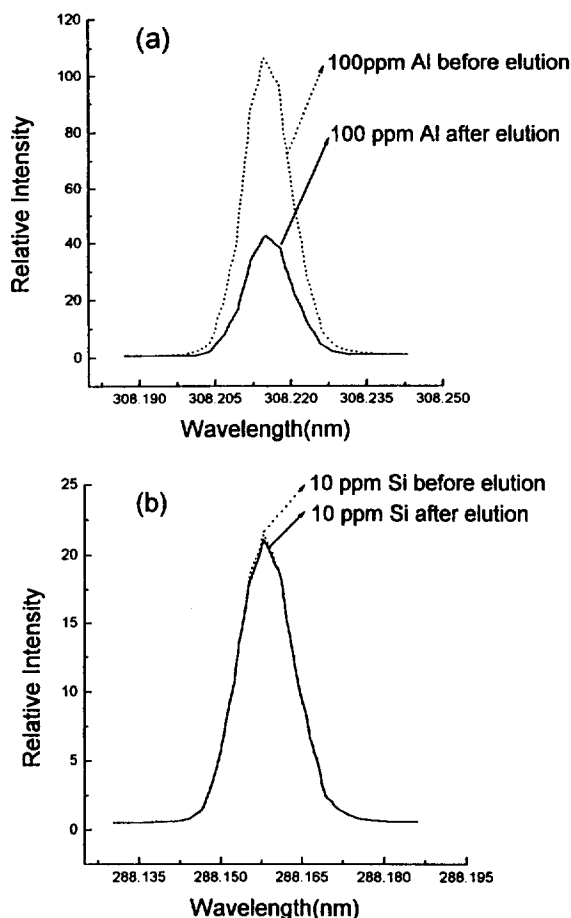
Figure 1. Spectrum of 100 μg mL^{-1} of Al (a) and 10 μg mL^{-1} of Si (b) before and after the elution.

Table 1. Experimental results of recovery test after separation of Si from Al

Sample fraction[a]	Al (recovered, %)				Si (recovered, %)		
	sulfuric acid (v/v)				sulfuric acid (v/v)		
	7%	2%	0.4%	0.08%	2%	0.4%	0.08%
1st	30.9						
2nd	80.4	0.3	0.1	0.03	90.1	92.7	94.4
3rd	91.1	0.3	<0.01	<0.01	92.6	93.5	94.4
4th		0.4	0.05	<0.01	91.9	93.2	94.0
5th		0.5	0.07	0.02	93.0	91.8	94.7
6th		0.8	0.06		93.4	92.7	

[a]Each fraction contains 20 mL of the sample.

The spectrum was obtained in the condition of 2% (v/v) conc. sulfuric acid with about 20 mL of resin without using any precolumn. From the spectrum, the signal of aluminium after the elution was reduced significantly compared to that before the elution, while the intensity of silicon was unchanged. It clearly proved that Al matrix can be removed without any loss of the trace amount of Si analyte for employing the selected ion exchange resin.

Optimization of the procedure. It is well known that concentration of acid is one of the most important factor to control separation efficiency and retention time in ion exchange process. In this experiment sulfuric acid used to decompose Al$_2$O$_3$ powder was chosen to see the effect of the concentration on the efficiency of matrix removal. Since the final concentration of conc. sulfuric acid was about 1.0 to 4% (v/v) for the high pressure acid digestion bomb method optimized in the previous experiment, the prepared concentrations of sulfuric acid in this experiment range from 0.08% to 7%.

The volume of the resin for precolumn and separation column was sufficiently enough to eliminate all the Al matrix from the 200 mL of prepared sample solution. In order to check the dilution effect due to the presence of the volume placed on the resin before the elution, the samples were taken every 20 mL from the exit of separation column for various concentrations of sulfuric acid. For the precolumn elution first 50 mL of sample was discarded by the same reason, so that the sample volume was reduced to about 150 mL after precolumn. Under the optimized conditions used, the recoveries of Si and Al were obtained as shown in Table 1. As shown in the table, the first fractions of 20 mL for each sulfuric acid concentration except 7% were not measured because it is expected to be diluted due to the preoccupied volume.

From the table, it could be concluded that the percentage of recovery for Al, that is, not filtered but remained in the solution after elution, increased as the concentration of the acid increased. It is special to say that the increment was very sharp after 2% of sulfuric acid. If acid concentration was less than 2%, over 99.5% of Al can be eliminated from the solution. It is of course desirable to obtain the lower recovery of Al and the higher for Si for the better efficiency of Al matrix removal. Therefore, it would be better to make the final acid concentration of less than 2% when dissolving

rapid sequential spectrometer was used for wavelength selection. Another model of ICP-AES for confirmative experiment is a sequential ICP-AES (ARL 3410, 27 MHz, ARL Applied Research Lab. S.A., Switzerland) operated at 0.6 kW forward power with a coolant flow of 8 l min.$^{-1}$, a nebulizer flow of 0.6 l min.$^{-1}$, and sample uptake rate of 2 mL min.$^{-1}$ adjusted with the peristaltic pump.

Results and Discussion

Matrix elimination procedure. It is certain that the separation of Si to be determined from Al matrix improve the power of detection for Si in ICP-AES. The Al matrix matching for preparing standard solution, which is tedious and time-consuming process, was not necessary and spectral interference due to the presence of aluminium in excess can be eliminated.

Most of Si dissolved in the presence of excess Na is expected to be as negative charge, but aluminium dissolved in sulfuric acid solution will have an opposite charge. Therefore, when the solution containing Si in the aluminium matrix was eluted, only silicon past through the column packed with cation exchange resin while the matrix would be held in the resin and removed.

In Figure 1 shown are the spectrum of about 100 μg mL^{-1} of Al and 10 μg mL^{-1} of Si before and after the elution.

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Notes

Table 2. The results of Si analysis in Al_2O_3 with matrix matching technique and matrix removal   unit : μg/mL

Sample	Matrix matching	Matrix separation
#1	15.5	12.0
#2	25.3	18.6
#3	91.8	81.9

ceramic samples using high pressure acid digestion bomb method.

The recovered percentages of Si over all acid concentrations prepared was over 90% with the relative standard deviation of less than 1.5%. Even there was some loss of Si for the acid concentration range of 0.08% to 2%, the recovery was fairly reproducible. The loss can cause the decrease of Si signal from the true value. Another thing to point out in this experiment is that about 20 to 40 mL of the front part of the collected solution from the separation column should be discarded because it was found that the recovery of Si increased from about 30% at first 20 mL of the solution to about 91% at 60 mL in the sulfuric acid concentration of 7%. Such results, *i.e.*, loss of Si and dead volume occurring during the matrix elimination process, mean that large volume of sample was required for the quantitative analysis with good reproducibility and precision.

From the results, it should also be noted that acid concentrations have influence on not only the signal intensity in ICP-AES but also the efficiency of matrix removal. When sulfuric acid was added to decompose the fine ceramic powder of Al_2O_3, the volume should be controlled considerably. If too much acid was added, the decrease of removal efficiency would be expected besides the signal suppression due to the presence of sulfuric acid in ICP-AES. On the other hand, in case that too small amount of acid was used, much longer time is required to decompose sample powder and even no complete dissolution can be accomplished.

Application to Al_2O_3 ceramics. The Al matrix elimination method was applied to the real ceramic powder and the analytical results for Si are shown in Table 2. The result was compared with that of matrix matching technique. From the table it is general to say that matrix elimination technique gave less analytical value than matrix matching technique. However, this method does not require to prepare Al matrix matched standard solution that is known to be time consuming and laborious works in the laboratories. Therefore, it will be useful to apply this method to the industrial laboratories in which many samples are to be handled daily.

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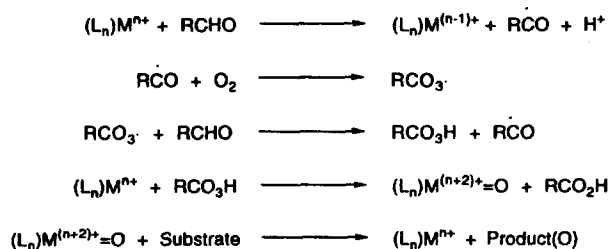# Nickel Complex as a Radical Inhibitor in the Oxidation Reactions by Dioxygen Plus Aldehyde

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Catalytic oxidation of hydrocarbons by dioxygen plus aldehyde catalyzed by metal complexes is of current interest in functionalization of organic compounds.[1] These reactions proceed *via* a free-radical type of mechanism in which radicals such as acyl and acylperoxy radicals are generated in the reaction media (Scheme 1).[1(a),2] While we have been studying the epoxidation of olefins by dioxygen plus aldehyde in the presence of metal complexes,[3] we found that nickel complexes of tetraazamacrocyclic ligands have the ability to inhibit the radical type of oxidation reactions.[4] We herein describe the inhibition of the radical reaction by a

$$(L_n)M^{n+} + RCHO \longrightarrow (L_n)M^{(n-1)+} + R\dot{C}O + H^+$$

$$R\dot{C}O + O_2 \longrightarrow RCO_3^{\cdot}$$

$$RCO_3^{\cdot} + RCHO \longrightarrow RCO_3H + R\dot{C}O$$

$$(L_n)M^{n+} + RCO_3H \longrightarrow (L_n)M^{(n+2)+}=O + RCO_2H$$

$$(L_n)M^{(n+2)+}=O + Substrate \longrightarrow (L_n)M^{n+} + Product(O)$$

Scheme 1.