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## Development of Continuous Flow Microwave Digestion Procedures for Analysis of Trace Metal Oxides in Water Using Ion Chromatography

Youn Doo Kim<sup>†</sup>, Gae Ho Lee, Hyung Seung Kim, Dong Soo Kim, and Kwang Kyu Park<sup>\*</sup>

<sup>\*</sup>Department of Chemistry, Chung-Nam National University, Daejeon 305-764, Korea

<sup>†</sup>Water chemistry team, Research Center, Korea Electric Power Corporation Daejeon, 305-380, Korea

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A simple and rapid sample pretreatment process necessary for determination of metal oxides in water was proposed. Samples were injected into the continuous-flow tube installed inside the microwave oven and the treated samples were cooled before entered to the Ion Chromatography (IC) or Inductively Coupled Plasma (ICP). By coupling this microwave digestion system with IC or ICP, a fully automatic analytical procedures may be easily established. In this study, two different types of digestion methods were considered; the open tubing method (OTM) and the restraint tubing method (RTM). The RTM was proved to be 3 times faster in digestion period and 10 times higher in detection range than the OTM. Validation of proposed sample digestion system was carried out by using an ICP. The results showed that both of continuous-flow methods, the OTM and the RTM were comparable in accuracies with the conventional batch-type vessel digestion method.

### Introduction

While there have been significant advances in analytical instrumentation in these days, sample pretreatment procedures haven't been much changed. The power of analytical instrumentation has been further enhanced by the introduction of computer-based operating systems.

On the other hand, digestion techniques have remained relatively static over recent years and are now clearly the most time-consuming and error-prone step in the procedure. Conventional methods, such as hot-plate acid digestions are time consuming, subject to thermal gradients across the hot-plates or hot blocks, susceptible to airborne and cross contamination as well as the mechanical loss of analytes of interest.<sup>12</sup>

The application of a microwave radiation field as an energy source for sample digestion was reported about 20 years ago for the first time.<sup>3,4</sup> This technique seems to have been largely unnoticed until 1985 when the interest in microwave digestion became very popular.<sup>5-9</sup> To date, the majority of digestions described have been based upon a batch technique, in which the microwave digestion replaces traditional wet or dry ashing methodology.<sup>10-13</sup> The move to microwave digestion approach offers many advantages over the conventional methods including reduction in digestion time, digestion of difficult matrices and dissolution in what is essentially a closed environment, which reduces volatile analyte's loss and atmospheric contamination. Despite these obvious advantages, the batch type of approach to sample digestion to be prone to contamination problems associated with the sample, reagent and containment together with analyte's loss

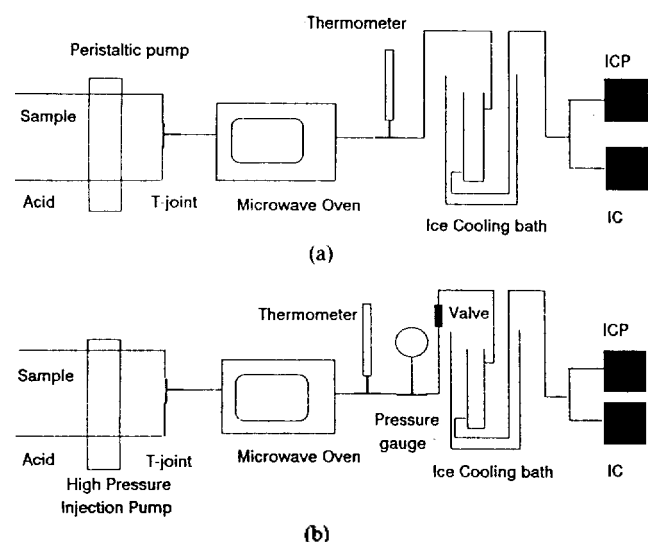
and potential errors from volumetric transfers is still used. Sample preparation still remains a multi-step and labour-intensive procedure. Many of these problems can be overcome or controlled by adopting a flow injection (FI) methodology. There have been only a few reports of systems based upon this approach until now, which has been successful with blood samples.<sup>14</sup> Other approaches employ stopped-flow systems in order to obtain a solid-free acid solution from biological samples.<sup>15-18</sup>

The goal of this work is to develop a simple and inexpensive system for the on-line microwave digestion of metal oxides in boiler water of power plant. The injected sample is dissolved in the flow system of a domestic microwave oven. The metals are determined by ion chromatography and the results of IC were compared with those of ICP-AES. Analytical results for boiler feed water of Seochon thermal power plants which is located in the West seaside in Korea are presented herein.

### Experimental

#### Apparatus

A schematic diagram of lab-constructed open and restraint tubing digestion system is shown in Figure 1. Both systems were assembled as follows: (i) sample introduction part, Gilson M312 peristaltic pump for open tubing digestion system and Milton high pressure injection pump for restraint tubing digestion system; (ii) domestic microwave oven (Samsung electrical Co.); (iii) cooling system; (iv) teflon coated thermometer and pressure sensor and pressure regulator valve of Cole-Parmer Co. for restraint tubing system; (v) Nalgene



**Figure 1.** Schematic Diagram of the Continuous Flow Microwave Digestion. (A) Open Tubing Digestion System (B) Restraint Tubing Digestion System.

**Table 1.** Instrumental Parameters and Analytical Conditions for IC Analysis

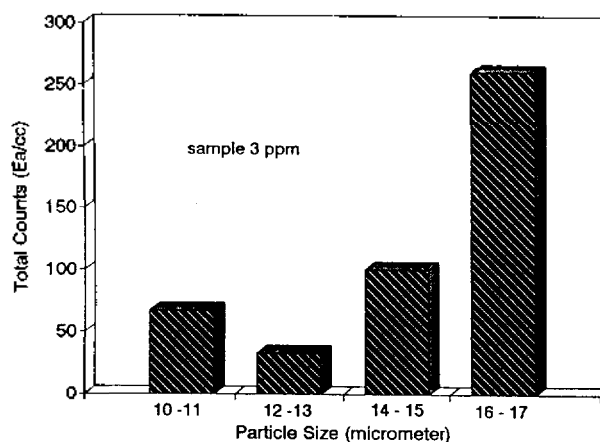
Ion Chromatograph	Dionex 4000i
Sample Loop Volume	500 $\mu$ L
Separator Column	HPIC-CS5 (4 mm ID $\times$ 50 mm)
Detector	UV Detector
Eluent	6 mM PDCA 50 mM Acetic Acid 50 mM Sodium Acetate Trihydrate
Eluent Flow Rate	1.0 mL/min
Mixing Device	Membrane Reactor
Post Column Reagent	0.2 mM PAR 1 M Acetic Acid 3 M Ammonium Hydroxide
Reagent Flow Rate	0.7 mL/min
Detector Wavelength	520 nm

PTFE (Poly Tetra Fluoro Ethylene) tubing (1/16" *i.d.*).

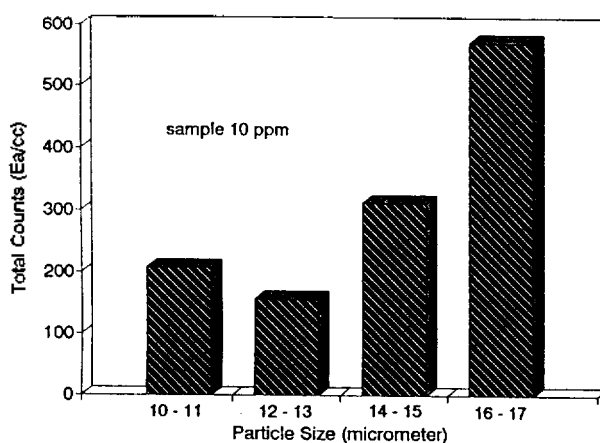
Digestion tube was wound around 1 L Pyrex cylinder to consider the geometry of the tubing and set in microwave cavity. This loop was introduced through the vent holes of the microwave oven. A cooled sample cell consisted of tube-coiled 50 mL cylinder in 1 L beaker and was equipped with a continuous ice-cooled recycling system. Digested sample was detected using Dionex 4000i Ion Chromatograph and Spectro Inductively Coupled Plasma (Germany). Experimental conditions are reported in Table 1.

#### Reagents and Samples

Concentrated hydrochloric acid and nitric acid were purified with sub-boiling distillation system (Karl Kolb, Germany) and the water used was distilled and de-ionized water with Barnstead Milli Q system. All metal oxide powders used were analytical-reagent grade supplied by Junsei Chemical Co. Standard solutions were prepared of our own because there was no standard solutions that the particulates of metal



**Figure 2.** Particle Size Distribution in 3 ppm Sample.



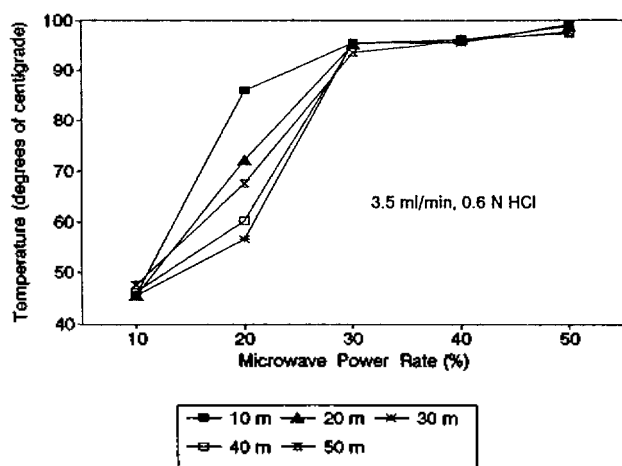
**Figure 3.** Particle Size Distribution in 10 ppm Sample.

oxide were distributed homogeneously in. Metal oxides chosen were  $Fe_3O_4$ ,  $CuO$ ,  $ZnO$  and  $CoO$  which were compositions of industrial facilities. Standard solutions were prepared by mixing metal oxide with de-ionized water, settling for one day and filtering with 5A filter paper (Toyo Roshi Kaisha Ltd. Japan). Among them, particle size and distribution of  $Fe_3O_4$  sample was frequently examined with Particle Counter (Spectrex SPC-510, USA). Figure 2 and 3 show that standard solution was made up of 10-17  $\mu$ m particulates.

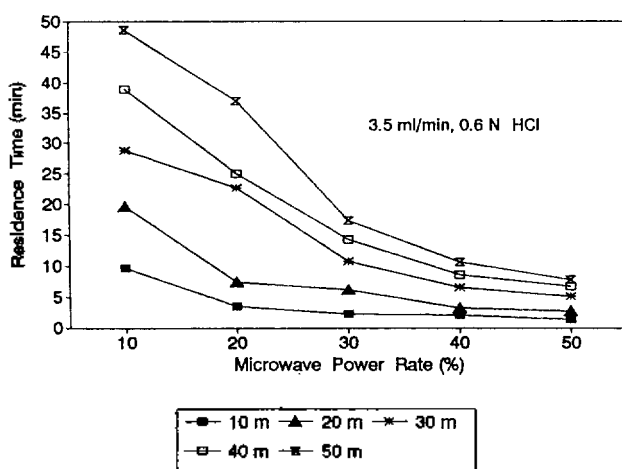
#### Procedures

**Open Tubing Digestion System.** This digestion system was tested to find the optimum conditions based on two variables such as microwave power rate and tube length. Temperature was measured using teflon coated thermometer of Cole-Parmer Co. and was held in the end of the digestion tube with a T-joint (Figure 1). The results for various power rate and tube length on the temperature under the condition of 3.5 mL/min of flow rate and 0.6 N HCl were shown in Figure 4.

The residence time in various tube length depended on the microwave power rate. The results were shown in Figure 5. As the tube length was increased, the carrier stream flow rate were also increased to keep the residence time constant. Below 20 minutes, poor results were obtained because of incomplete acid attack. When the residence time was longer



**Figure 4.** Temperature of Solution in each Tube at various Power Rate.

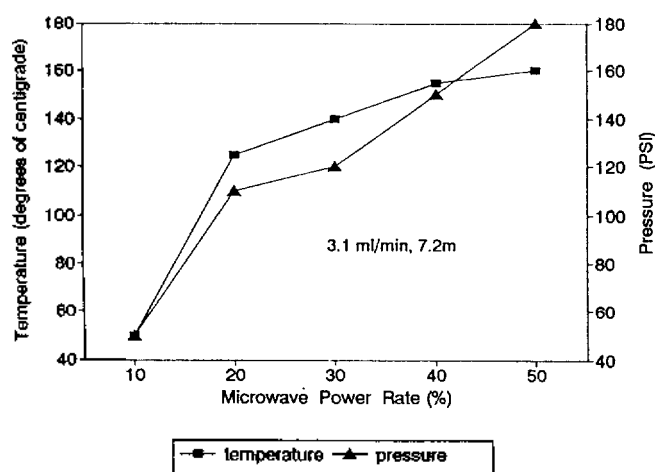


**Figure 5.** Residence Time of Solution in each Tube at various Power Rate.

than 30 minutes, the carrier solution flow pattern started to be attacked by gas evolution, probably from fume generated during the dissolution. A blue-colored dye (Methylene Blue) was used to determine the sample residence time. Prior to injection of samples through microwave oven, the digestion tube was flushed by pumping with an acid mixture (HCl 1+1), because some of the materials adhered to the inner walls of the tubes, output valve, T-joint and trace element accumulated gave rise to memory effect.

Synthesized standard samples were continuously and vigorously stirred and pumped into the digestion tube simultaneously with an acid. After digestion, the sample was passed into water cooling system. The effluent was wasted for 20 minutes in initial stage and then quantitatively transferred into the collection vessel. In the initial stage, sample with residues was filtered using a Nalgene handy pump and the filtered particulates on Millipore membrane filter (0.45  $\mu\text{m}$  pore size) were investigated with optical microscope. The final dissolved solutions were then analyzed by Ion Chromatography and ICP-AES.

**Restraint Tubing Digestion System.** This system



**Figure 6.** Temperature and Pressure in Restraint System at various Power Rate.

was modified by attaching an discharge valve at the end of a digestion tube to keep high pressure in digestion tube. Unlike other workers who measured temperature in real time during the course of digestion, the initial concern of this study was the final temperature of the sample rather than a temperature versus time profile. Temperature and pressure were monitored using a teflon coated thermometer and pressure gauge in order to establish the operating conditions at which the tube assembly can be operated safely. The temperature and pressure at various microwave power rates, under the condition of 3.1 mL/min of flow rate and 7.2 m of tube length were shown in Figure 6. Digestion procedure such as sample injection, digestion, cooling and detection was performed in the same way with open tubing digestion system. Taking into account of the reproducibility of this system, the control of the discharge valve at the end of the digestion tube is very important.

#### Safety Considerations

Owing to the potentially hazardous microwave energy and acids at elevated pressure and temperature, safety was a key consideration in operating this system. The domestic microwave oven was used without any modification. The use of vent holes of the oven to serve as entrance and exit points for the digestion coil avoids problems related to radiation leakage and exposure of the operator to the microwave radiation. Microwave leakage was extensively tested using microwave Survey Meter (Holaday Industries, Model HZ 1501; detection limit 0.01 mV). The measured values were found to be less than 0.2 mV/cm<sup>2</sup> at vent area. Those values are much lower than domestic guide line of 5 mV/cm<sup>2</sup> being found at a distance of 5 cm front the oven.

#### Results and Discussion

The solubilities with batch-type desolvation system are increased by increasing microwave power rate, but the solubilities with flow-type desolvation system show a different tendency. In general, digestion conditions or degree of dissolution in microwave cavity were governed by four variables in both systems, such as microwave power rate, tubing length, concentration of acid and flow rate.

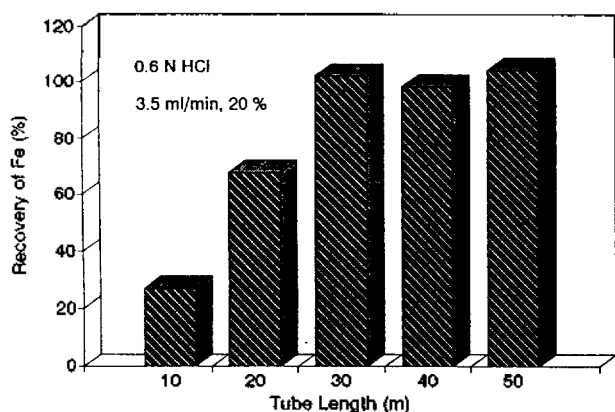


Figure 7. Effect of Tubing Length on the Recovery of Fe(%) in Open System.

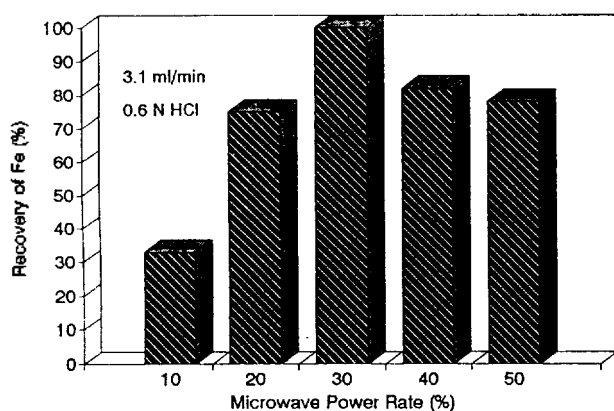


Figure 8. Effect of Microwave Power Rate on the Recovery of Fe(%) in Restraint System.

The sample residence time is the most important factor in OTD. Since the sample residence time is greatly affected by all four variables mentioned above, the four variables have to be controlled properly in order not to make any bubbles inside the tube or to be maintained at high temperature. The dependency of four variables on degree of dissolution was investigated thoroughly. Among them, the dependency of tube length on the degree of dissolution is shown in Figure 7. The five different lengths of tubing (10, 20, 30, 40 and 50 m) were used at 20% microwave power rate, 3.5 mL/min flow rate and 0.6 N HCl. In 20 and 10 m of tube length, poor results were obtained like 70 and 30% respectively because of insufficient residence time. It was found that at lengths greater than 30 m, the solution in digestion tube started to be affected by gas evolution and degraded the reproducibility. Finally 30 m of tube length was optimized to achieve satisfactory mineralization.

On the other hand, the restraint tubing digestion system was designed to overcome the defects of the open tubing digestion system, such as long digestion time and small amount of sample to be digested. Discharge valve was placed near the end of tube to make temperature and pressure much higher. The effect of microwave power rate was also examined under the condition of 0.6 N HCl, 7.2 m tube length and 3.1 mL/min flow rate. Power rates were varied in

Table 2. The Optimum Conditions of OTM and RTM

Items	OTM	RTM
Microwave Power Rate	20%	30%
Flow Rate	3.5 mL/min	3.1 mL/min
Acid Concentration	HCl: 0.6 N HNO <sub>3</sub> : 2.5 N	HCl: 0.6 N HNO <sub>3</sub> : 1.5 N
Tubing Length	30 m	7.2 m
Instrument	Ion Chromatography Inductively Coupled Plasma Spectroscopy	Ion Chromatography Inductively Coupled Plasma Spectroscopy

(Note; OTM-Open Tubing Method, RTM-Restraint Tubing Method)

the range of 10-50%. The result was shown in Figure 8. At higher power rate than 40%, gas formation in digestion loop was observed and pressure overran the safety operating conditions. It gave rise to shorter residence time, unstable temperature profile, ever-changing pressure to open the discharge valve so as to establish the safety pressure. The optimum power rate was found to be 30%.

**Optimization of Digestion Conditions.** The open tubing and the restraint tubing digestion methods for flow injection were designed and tested to find the optimum conditions. The results were listed in Table 2. The total analysis time including digestion and detection were 37 minutes in the open tubing digestion system and 23 minutes in the restraint tubing digestion system under the determined optimum digestion conditions. The maximum concentrations of samples which can dissolve using the open and the restraint tubing digestion systems were 1.5 ppm, 15 ppm, respectively.

**Precision and Accuracy.** The recovery of each metal was determined by the developed methods on standard samples. To check the accuracy of these methods, the sample also digested by a teflon open vessel which is commercialized and popular for digestion of metals. The metals were determined by IC and also analyzed by ICP-AES. The similar analytical results were obtained. The results, summarized in Table 3, showed satisfactory precision. Fe and Cu shows good precision with approximately 6% RSD, while Zn and Co more or less than 10% RSD. The open tubing digestion system showed same results as the restraint tubing digestion system.

**Ion Chromatography (IC).** Metal ions are usually determined by spectroscopic instruments with good precision, however they are too much expensive in both installation and operation. IC has rapidly advanced since its introduction in 1975. The technique was originally used to separate anions and alkaline-earth metals. But there have been only a few reports to separate transition metals by IC. Thus digested samples analyzed by IC and its results are compared with that of ICP-AES. The results of analysis by both IC and ICP-AES listed in Table 4. The results of IC agreed with those of ICP with less than 3% deviation. It is concluded that IC monitoring system is less expensive for installation and operation than ICP-AES. However, the presence of mineral acids in IC is more critical in matrix effect than that of ICP-AES.

Interferences caused by low concentration of mineral acids

**Table 3.** Results obtained in the determination of Fe, Cu, Zn and Co

(Concentration : mg/L)

Run No.	Batch Type				Open Tubing Method				Restrained Tubing Method			
	Fe	Cu	Zn	Co	Fe	Cu	Zn	Co	Fe	Cu	Zn	Co
1	1.739	1.253	1.080	0.367	1.612	1.423	1.058	0.386	1.786	1.411	0.915	0.355
2	1.759	1.422	1.102	0.360	1.759	1.421	1.144	0.351	1.907	1.448	1.239	0.438
3	1.537	1.461	1.054	0.384	1.971	1.362	1.224	0.399	1.795	1.388	1.039	0.369
4	1.721	1.393	1.088	0.379	1.763	1.347	1.095	0.402	1.702	1.235	1.155	0.375
5	1.699	1.244	1.261	0.406	1.567	1.218	0.877	0.384	1.874	1.429	1.187	0.356
6	1.698	1.396	1.031	0.413	1.787	1.290	1.118	0.338	1.606	1.231	1.061	0.361
7	1.817	1.330	0.989	0.340	1.548	1.345	1.134	0.439	1.711	1.365	1.112	0.374
8	1.939	1.409	0.970	0.439	1.923	1.438	0.909	0.409	1.613	1.394	0.871	0.420
AVG	1.739	1.364	1.072	0.386	1.741	1.356	1.070	0.389	1.749	1.363	1.072	0.381
RSD (%)	6.1	5.5	7.8	7.7	8.4	5.2	10.4	7.7	6.0	5.8	11.2	7.6

(Note: These results were determined by IC and confirmed by ICP-AES in 0.6 N HCl)

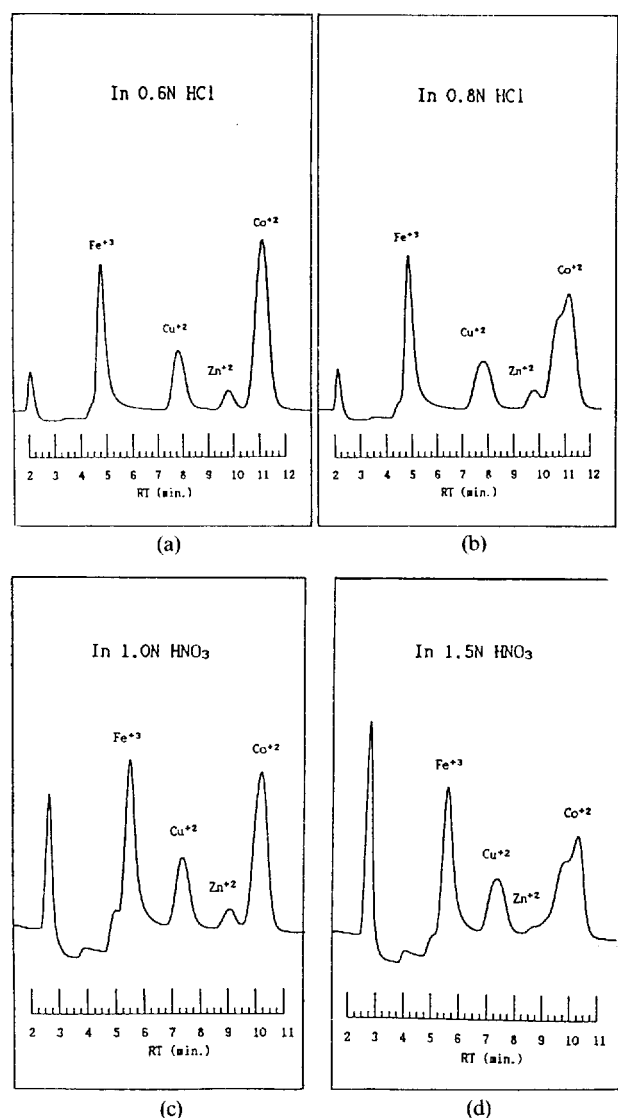
**Table 4.** Metal Ion Concentration in the prepared samples determined by IC and ICP

Run No.	Fe (mg/L)			Cu (mg/L)		
	IC	ICP	IC/ICP	IC	ICP	IC/ICP
1	1.917	1.798	1.066	1.432	1.438	0.996
2	1.905	1.807	1.054	1.422	1.450	0.981
3	1.879	1.804	1.042	1.426	1.443	0.988
4	1.873	1.803	1.039	1.416	1.445	0.980
5	1.881	1.794	1.049	1.402	1.437	0.976
6	1.758	1.790	0.982	1.433	1.434	0.999
7	1.839	1.784	1.031	1.431	1.438	0.995
8	1.839	1.789	1.028	1.426	1.437	0.992
AVG	1.861	1.796	1.036	1.424	1.440	0.988
STD	0.047	0.008	0.024	0.010	0.005	0.008
RSD (%)	2.5	0.4	2.3	0.7	0.3	0.8

**Table 5.** Analytical results for Seocheon T/P boiler water by proposed procedure

(Microwave Digestion System+IC or ICP)

Run No.	Fe (mg/L)			Cu (mg/L)		
	IC	ICP	IC/ICP	IC	ICP	IC/ICP
1	0.781	0.691	1.130	0.875	0.871	1.005
2	0.731	0.700	1.044	0.854	0.875	0.976
3	0.736	0.692	1.064	0.861	0.875	0.984
4	0.739	0.689	1.073	0.910	0.873	1.042
5	0.746	0.697	1.070	0.872	0.873	0.999
6	0.735	0.690	1.065	0.853	0.869	0.982
7	0.732	0.689	1.062	0.901	0.873	1.032
8	0.733	0.691	1.061	0.869	0.860	1.011
AVG	0.742	0.692	1.071	0.874	0.871	1.004
STD	0.016	0.004	0.024	0.020	0.005	0.022
RSD (%)	2.1	0.5	2.2	2.2	0.5	2.2

**Figure 9.** Ion Chromatogram for the Analysis of prepared Samples in HCl and HNO<sub>3</sub>. (a) Chromatogram in 0.6 N HCl (b) Chromatogram in 0.8 N HCl (c) Chromatogram in 1.0 N HNO<sub>3</sub> (d) Chromatogram in 1.5 N HNO<sub>3</sub>.

have been investigated in IC. Acid species are hydrochloric acid and nitric acid. Acid content in standard sample are adjusted from 0.2 N to 1.0 N for HCl, and from 0.2 N to 2.5 N for HNO<sub>3</sub>. Significant effect was observed at the concentration above 0.8 N for HCl and 1.5 N for HNO<sub>3</sub> as shown in Figure 9. Chromatograms showed broadening and splitting pattern due to the high concentrations of acids. Therefore the influence of the acid cannot be considered negligible, although further work is needed.

**Analysis of real sample.** In order to evaluate on the developed digestion system, boiler feed water of Seocheon power plant located in the West coast were digested and analyzed. The results are shown in Table 5 with good precision. Results show high concentration of Fe and Cu, because Seocheon power plant was operated again after a long shutdown. The concentration of Cu higher than that of Fe indicates needs of more examination of its boiler system.

### Conclusion

The method described offers rapid and efficient sample preparation using microwave digestion for the determination of metal oxides in boiler feed water of power plants. The microwave digestion system reduces sample handling and make complete automation of the analysis possible. The open tubing method (OTM) and the restraint tubing method (RTM) were designed for microwave digestion system and tested to find the optimum conditions. RTM was 3 times quicker on the digestion time and 10 times higher on sample mass. The results of RTM agree well with those by conventional microwave open vessel in all cases; Fe and Cu show good agreement within about 6% of RSD, while Zn and Co more or less than 10% RSD. The concentration of samples analyzed by IC and compared with those of ICP-AES. The results of IC agree with those of ICP with less than 3% deviation. According to this study, the continuous flow microwave digestion system provides the proper dissolution method for the analysis of solid particulate sample directly in

IC or ICP-AES.

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## Conformations of 25,27-Diacyloxy-26,28-dialkyloxy-calix[4]arenes

Kwanghyun No\*, Hee Jung Koo and Min Seong Lee

Department of Chemistry, Sookmyung Women's University, Seoul 140-742, Korea

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1,3-Dimethyl and dipropyl ethers of *p*-*t*-butylcalix[4]arene and calix[4]arenes have been converted to the corresponding diesters, acetate and propionate, and their conformations are inferred based on the <sup>1</sup>H and <sup>13</sup>C NMR spectra. The presence of *t*-butyl groups is effective in maintaining the cone conformation on derivatization.

### Introduction

Calixarenes, a class of synthetic macrocycles having phenolic residues in a cyclic array linked by methylene groups at the positions "ortho" to the hydroxy groups, have cavities

of sufficient size to form host-guest complexes, thus, are particularly attractive compounds for attempting to construct systems that mimic the catalytic activity of the enzyme and have received a great deal of attention in recent years<sup>1,2</sup>.

The cavity of calixarene is conformationally mobile and