Mass Background Spectra of ICP-MS with Various Acids

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Background spectra of ICP-MS performed with acid can interfere with the spectra of sample analytes. Thus, we have investigated the background spectra of various acids for use in elemental analysis by argon inductively coupled plasma mass spectrometry. The background spectra for 2% HNO_3, 5% HNO_3, 5% H_2SO_4, and 4% CH_3COOH were obtained with ICP-MS. This study also shows the possibility of the interference of Na, which could not be from the matrix, but from the ICP-MS sampler. The source of interference of boron was the vibrating glass surface of ultrasonic nebulizer. After a mug cup was kept in 4% CH_3COOH for 24 hours, trace Pb was determined with ICP-MS.

Key Words : ICP-MS, Acids, Background, Spectra

Introduction

Ar inductively coupled plasma (Ar ICP) was joined with a mass spectrometer by Houk *et al*.[1] Since then, argon inductively coupled plasma mass spectrometry (Ar ICP-MS) has been the most powerful technique for trace and ultra trace elemental analysis. This analytical technique provides excellent detection limits (parts per trillion range) and wide dynamic ranges for most elements.[1,2] Isotopic information can be obtained from it and its background spectra are relatively simple. These characteristics result mainly from the unique properties of the Ar ICP: high gas and electron temperature, high electron number density, and annular configuration.[2] In Ar ICP-MS, the solution sample is converted into an aerosol *via* a nebulizer, and then introduced into the plasma for vaporization, atomization and ionization. The ionized species in the plasma are extracted into the mass spectrometer and detected on the basis of their mass to charge ratio.[1-6]

One of the most critical steps in spectrometric methods is the introduction of the sample into the plasma. The most common sample introduction systems are the pneumatic nebulizer, PN, and ultrasonic nebulizer, USN. The pneumatic nebulizer's simplicity and low cost have made it the most widely used of the two. The concentric-nebulizer and cross-flow nebulizer belong to the pneumatic category. Because it enhances sensitivity in ICP spectrometry, the ultrasonic nebulizer is a popular method for sample introduction even though it is costly.[7-14]

In the present study, evaluations of Ar ICP-MS (Thermo Elemental) background spectra were performed for dry plasma, deionized water, 2% nitric acid, 5% hydrochloric acid, 5% sulfuric acid, 4% acetic acid, and 5% nitric acid because various samples, such as food, are typically decomposed with heat (dry-ashed) and dissolved in acids before introduction into the plasma. In ICP-MS, the characteristics of background spectra are important because interference from the overlap of sample and matrix spectra could affect analyte signal intensities in trace elemental analysis. In particular, spectral interference also could affect isotopic ratio in the isotopic dilution technique. This study also shows that Na interference could be from sampler contamination.

Experimental

Instrumentation. ICP-MS (VG PQ Excell, Thermo Elemental, Franklin, MA, USA). Details of the instrumental and operating conditions are described in Table 1.

Reagents. Nitric acid was obtained from VHG Labs, Inc., Manchester, NH, USA. Acetic acid, Aldrich Chemical Company Inc., Milwaukee, Wis, USA. Hydrochloric acid and sulfuric acid, Dongwoo Fine-Chem Co., Kangnam-Gu, Seoul, Korea. All solutions were prepared with 18 MΩ·cm distilled deionized water obtained from the PURELAB Plus water purification system, ELGA, High Wycombe, U.K.

Results and Discussion

Background Spectra with Dry Plasma. The background spectra of ICP-MS were obtained for dry plasma, which is

Table 1. Instrumental and operating conditions

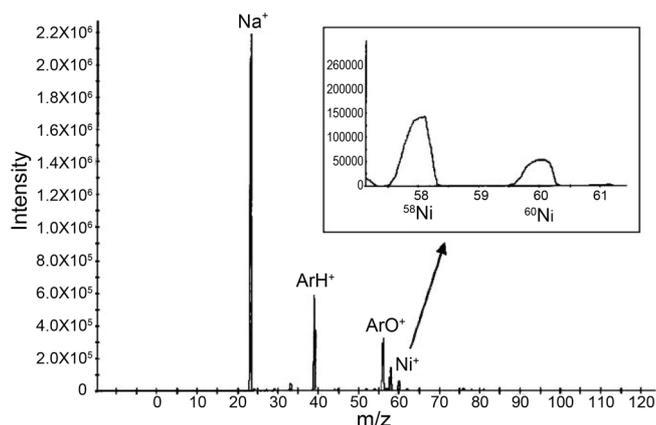|	
Sampling and skimmer cone	Nickel
Pneumatic Nebulizer (PN)	Concentric Nebulizer
	Impact bead spray chamber (3 °C water cooling)
Ultrasonic Nebulizer (USN)	desolvation unit, heating chamber 150 °C
	desolvation unit, condenser −5 °C
RF power	1350 W
Reflect power	1.2 W
Argon gas flow rate	
Coolant gas	13 L/min
Auxiliary gas	0.32 L/min
Nebulizer gas	0.90 L/min

Figure 1. Dry background spectrum.

the absence of a sample. (Figure 1). As the results show, peaks of Ni (m/z: 58, 67.77%) and Ni (m/z: 60, 26.16%) were recorded. The ICP-MS sampler and skimmer were made of a nickel, suggesting that the nickel might have come from the sampler. The ratio of the intensities of Ni (m/z: 58) and Ni (m/z: 60) is equal to the isotopic natural abundance of Ni. The peak for Na (m/z: 23) is also shown in Figure 1. The Na might be from the sampler. The result shows the sampler might be contaminated with trace sodium chloride. There were also peaks of $^{38}ArH^+$ and $^{40}ArO^+$.

Background Spectra with Wet Plasma by PN. Distilled deionized water was introduced into the plasma, and the background ICP-MS spectra were obtained (Figure 2). The peaks of oxygen products (O_2^+ and ArO^+) have clearly increased. The intensity of the peak by $^{40}ArO^+$ dramatically increased compared with that of dry plasma. The intensity of the peak by $^{38}ArH^+$ increased by a factor of three. There was still a peak by Na, which indicated the ICP-MS sampler was the source of the Na.

Background Spectra with Acids by PN. The background spectra of ICP-MS with pneumatic nebulizer were obtained (Figure 3) when 2% HNO_3 was introduced into the plasma. Nitric acids are often used to dissolve solid samples. The small peaks of products by nitrogen ($^{14}N^{16}OH^+$ and $^{14}N^{16}O^{16}O^+$)
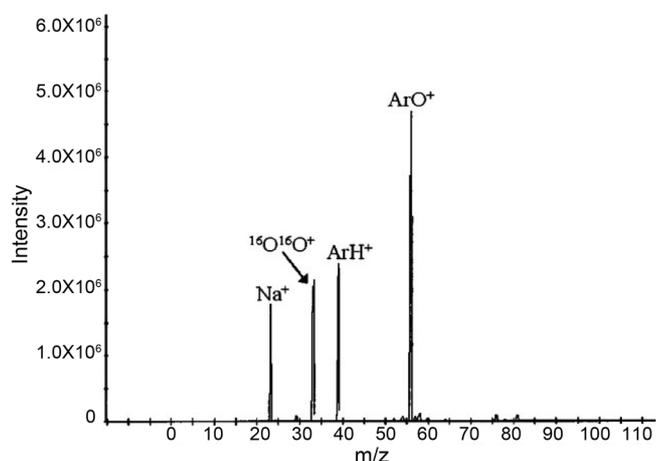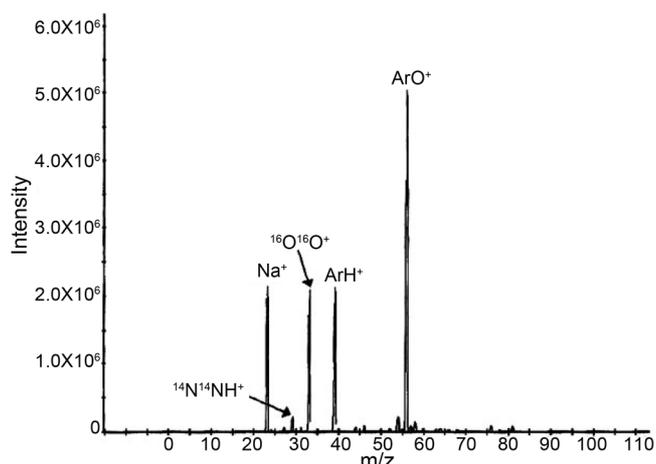

Figure 3. 2% HNO_3-PN background spectrum.

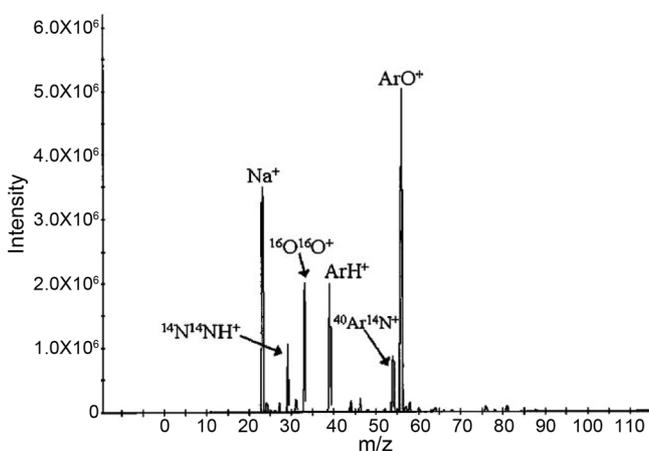**Figure 4**. 5% HNO_3-PN background spectrum.

are shown, in particular, the peak by $^{14}N^{14}NH^+$ is prominent. The intensities of peaks by $^{38}ArH^+$ and $^{40}ArO^+$ are comparable with those obtained with wet plasma by PN. The background spectra of ICP-MS with PN were obtained (Figure 4) when 5% HNO_3 was introduced into the plasma. The result shows the intensity of the peak by NNH^+ increased with the increased concentration of nitric acid. The peak
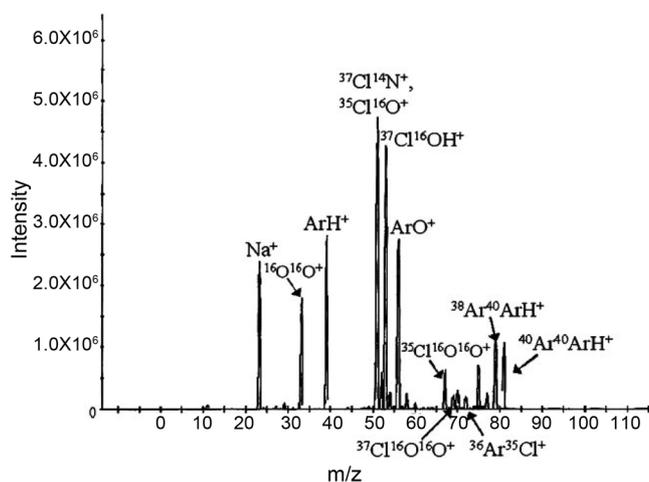

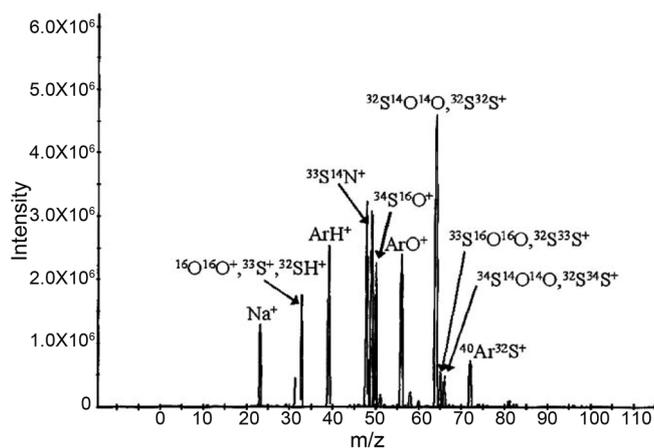**Figure 2**. DDW-PN background spectrum.

Figure 5. 5% HCl-PN background spectrum

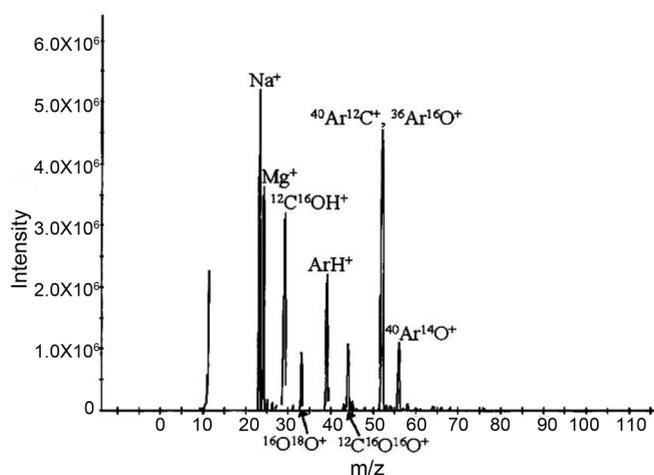**Figure 6**. 5% H_2SO_4-PN background spectrum.

Figure 7. 4% CH_3COOH-PN background spectrum.

by ArN^+ appears with 5% HNO_3, whereas it did not appear with 2% HNO_3.

The background spectra of ICP-MS with PN were obtained (Figure 5) when 5% HCl was introduced into the plasma. In general, the peaks of products by chlorine ($^{36}Ar^{35}Cl^+$, $^{37}Cl^{16}O^{16}O^+$, $^{35}Cl^{16}O^{16}O^+$, $^{37}Cl^{14}N^+$, $^{35}Cl^{16}O^+$, $^{37}Cl^{16}OH^+$) appeared. The peaks of products by Ar ($^{40}Ar^{40}ArH^+$, $^{38}Ar^{40}ArH^+$, $^{38}Ar^{38}Ar^+$, $^{36}Ar^{36}Ar^+$, $^{40}Ar^{14}N^{16}O^+$) were also clear, whereas they were not present with nitric acid.

The background spectra of ICP-MS with PN were obtained (Figure 6) when 5% H_2SO_4 was introduced into the plasma. In general, the peaks of products by sulfur ($^{32}S^{16}O^{16}O^{16}OH^+$, $^{34}S^{14}O^{14}O^+$, $^{32}S^{34}S^+$, $^{33}S^{16}O^{16}O^+$, $^{32}S^{33}S^+$, $^{32}S^{14}O^{14}O^+$, $^{32}S^{32}S^+$, $^{34}S^{16}O^+$, $^{33}S^{16}O^+$, $^{33}S^+$, $^{32}SH^+$) appeared. The peak by $^{40}Ar^{32}S^+$ was also clear. The background spectra of ICP-MS with PN were obtained (Figure 7) when 4% CH_3COOH was introduced into the plasma. The peaks of products by carbon and oxygen ($^{12}C^{16}OH^+$, $^{12}C^{16}O^{16}O^+$, $^{18}O^{16}O^+$) were recorded. The peak by $^{40}Ar^{12}C^+$ was also present. Also in this case, a 200 mL sample of 4% CH_3-COOH was kept in a cup for 24 hours, then the background spectra (Figure 8) were obtained and compared with the 4% CH_3COOH results above. Surprisingly, peaks for Pb were
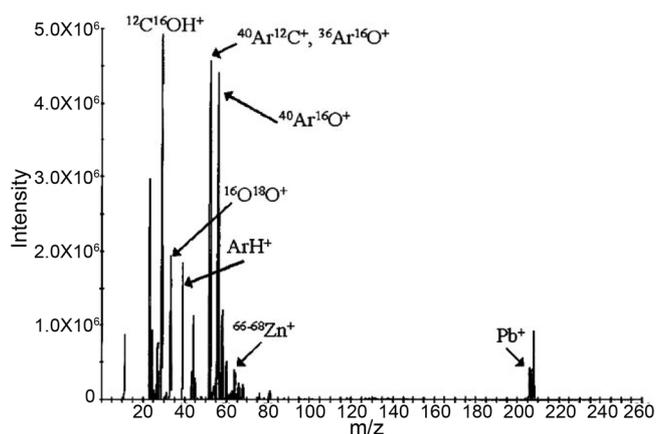

Figure 8. The determinations of elements released from mug into 4% acetic acid.

Table 2. The determination of Pb

Element	Mass	Concentration (ng/mL)
Pb	208	35.18 ± 3.2^a

[a]standard deviation of values measured three times

found. The amount of Pb released from the cup was determined by ICP-MS (m/z: 208). The result is shown in Table 2.

Background Spectra with Acids by USN. The background spectra of ICP-MS with ultra sonic nebulizer were obtained (Figure 9) when 5% HNO_3 was introduced into the plasma. The intensities of the peaks by $^{14}N^{14}NH^+$ and $^{40}Ar^{14}N^+$ were significantly increased, whereas the intensities of the peaks of $^{38}ArH^+$ and $^{40}ArO^+$ were reduced with USN compared with PN. The increases of the intensities of peaks by $^{14}N^{14}NH^+$ and $^{40}Ar^{14}N^+$ were due to the introduction of more analyte into the plasma with USN. In general, the detection capabilities of elements using USN coupled with ICP-MS were improved by a factor of ten compared with PN. The reduction of the intensities of the peaks of $^{38}ArH^+$ and $^{40}ArO^+$ indicate that less water was introduced into the plasma because of the USN desolvation system. A boron peak was clear. The boron might be from the USN vibrating glass surface.
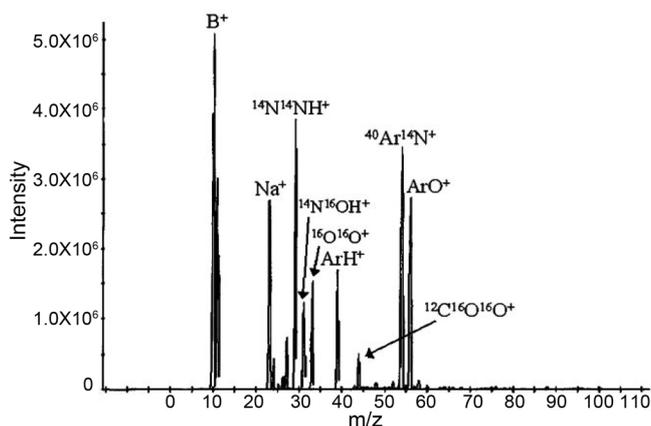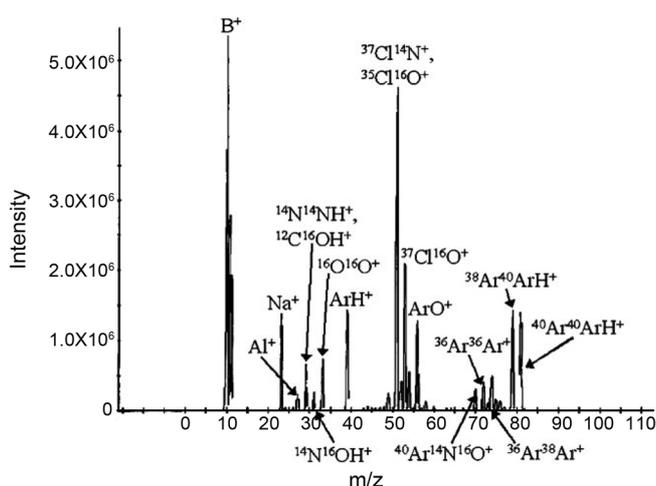

Figure 9. 5% HNO_3-USN background spectrum.

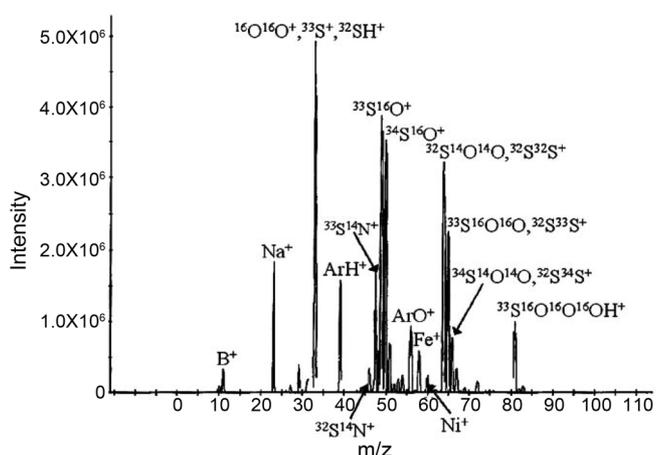**Figure 10**. 5% HCl-USN background spectrum.

Figure 11. 5% H_2SO_4-USN background spectrum.

Background spectra were obtained with 5% HCl by USN. The peak for B is similar to that of USN with 5% HNO_3. The results are shown in Figure 10. The intensities of $^{37}Cl^{16}OH^+$, $^{40}ArO^+$, $^{38}ArH^+$, and $^{16}O^{16}O^+$ were reduced with USN. The reduction might result from the USN desolvation system. Background spectra with 5% H_2SO_4 by USN are shown in Figure 11. The intensities of $^{40}ArO^+$ and $^{38}ArH^+$ fell with USN, whereas the intensities of $^{33}S^+$ and $^{32}SH^+$ were up significantly compared with PN. In general, the intensities of peaks for products of sulfur increased with USN. Figure 12 shows the background spectra with 4% CH_3COOH by USN. The peaks of Al, Ni and Zn increased because of the increased sensitivities with USN. There were still peaks for Na and B. In particular, the intensity of boron ion was significantly enhanced with USN.

Conclusion

Mass Background spectra for HNO_3, HCl, H_2SO_4 and CH_3COOH with Ar ICP-MS (pneumatic nebulizer and ultrasonic nebulizer) were successfully obtained and com-
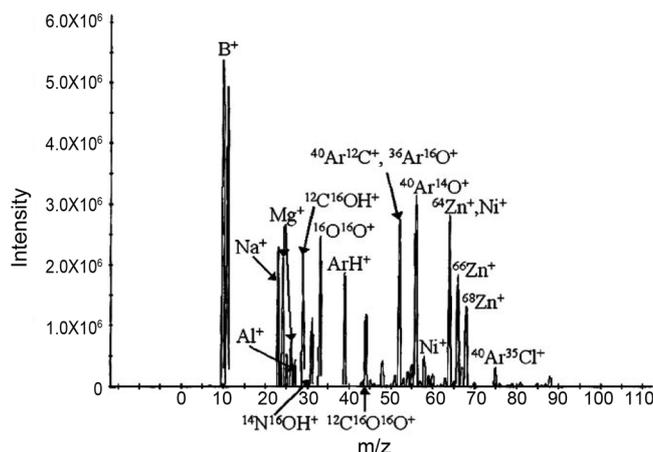

Figure 12. 4% CH_3COOH-USN background spectrum.

pared. Also, trace Pb released from a cup was found. 35 ng/mL Pb was determined in 4% acetic acid after the cup was leached in 4% acetic acid for 24 hours at room temperature. In general, the background spectra of Ar ICP-MS obtained by pneumatic nebulizer were simpler than those obtained by ultra sonic nebulizer. The spectral interferences of Na came from the sampler and the spectral interferences of B came from the ultrasonic nebulizer.

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