INTRODUCTION

Natural processes, deliberate addition, and inadvertent contamination during growth, processing, and preparation influence elemental levels in food materials. The nature and concentration of chemical elements found in foods are related to the biological role played by the elements in the tissue structure and physiology. Some of the elements such as Be, Pd, Cd, Hg, Tl, and Pb are regarded as toxic, several elements such as F, V, Cr, Mn, Co, Ni, Zn, As, Se, Mo, and Sn exhibit an essential/toxic duality (1).

Inductively coupled plasma mass spectrometry (ICP-MS) is a relatively new analytical technique which was developed in the 1980’s. ICP-MS combines the excellent ion source of an ICP and the ion detection capabilities of mass spectrometry, resulting in an analytical technique with many advantages, including: (a) most of elements in the periodic table can be determined, (b) high sensitivity, (c) rapid multielement analysis, (d) simple spectra, (e) wide linear range, (f) interferences can be predicted and corrected, and (g) the ability to determine the isotope ratio and perform isotope dilution analyses (2).

Much literature has been published discussing the determination of elements by ICP-MS. Crews (3) reviewed ICP-MS applications for food analysis in the first decade (1983–1993) of the development of this technique. Other literature (4–6) reported the determination of a number of elements in milk powders, including V, Mn, and Zn. Nikdel et al. (7) determined 10 elements in orange juice and grape fruit juice, including Mn, Zn, and Sn. Other elements such as V, Mn, Co, Zn, Mo, Cd, and Pb (2) and Hg (8) were determined in drinking water. Sheppard et al. (9) described the determination of As, Cd, and Pb in seafood products. Muto et al. (10) determined 13 elements in daily foods by ICP-MS, including Zn, Cr, As, Cd, Sn, Hg, Ti, and Pb. Alkanani et al. (11) compared analytical results obtained for the ICP-MS determination of 12 elements, including As, Cd, Cr, Mn, Mo, Ni, Zn, and Pb, in milk powder using different digestion procedures. Chou and Uthe (12) determined Ti and U in American lobster obtained from an industrialized harbor using ICP-MS. Salvato (13) determined Cd and Pb in 27 foods by ICP-MS.

This paper describes the development of an ICP-MS method for the simultaneous determination of 15 toxic elements (V, Cr, Mn, Co, Ni, Zn, As, Se, Mo, Pd, Cd, Sn, Hg, Ti, and Pb) in various foods and food materials such as belt-fish, beef, chicken stomach, pork liver, mussels, rice, corn flour, celery, shaddock, raw sugar, tea, grape juice, peanut oil, wine, spring water, and tap water. Certified reference materials of rice powder, pork liver, mussels, and milk powder were analyzed in this work for comparative purposes.

ABSTRACT

A method is described for the simultaneous ICP-MS determination of 15 toxic elements (V, Cr, Mn, Co, Ni, Zn, As, Se, Mo, Pd, Cd, Sn, Hg, Ti, and Pb) at trace levels in various foods. External calibration with Rh and Re as the internal standards was used. Reference materials were analyzed and the results compared with the reference values for the materials.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer SCIEX ELAN® 6000 ICP-MS (Perkin-Elmer SCIEX Instruments, Concord, Ontario, Canada) equipped with a Ryton® spray chamber and cross-flow nebulizer was used for all analyses. Table I lists the operating conditions employed for these experiments.

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>RF power</td>
<td>1000 W</td>
</tr>
<tr>
<td>Plasma Ar flow</td>
<td>15 L/min</td>
</tr>
<tr>
<td>Nebulizer Ar flow</td>
<td>0.8 L/min</td>
</tr>
<tr>
<td>Lens voltage</td>
<td>8 V</td>
</tr>
<tr>
<td>Analog stage voltage</td>
<td>–2750 V</td>
</tr>
<tr>
<td>Pulse stage voltage</td>
<td>1500 V</td>
</tr>
<tr>
<td>Sample uptake rate</td>
<td>1 mL/min</td>
</tr>
<tr>
<td>Scanning mode</td>
<td>Peak hopping</td>
</tr>
<tr>
<td>MCA channels per peak</td>
<td>1</td>
</tr>
<tr>
<td>Dwell time</td>
<td>100 ms</td>
</tr>
<tr>
<td>Total integration time</td>
<td>2 s</td>
</tr>
<tr>
<td>Number of replicates</td>
<td>6</td>
</tr>
</tbody>
</table>

Microwave processor from Hualing Ltd., Guangdong, P.R. China.

Reagents and Standard Solutions

Suprapure nitric acid: HNO₃ (reagent grade, Donghong Chemical Works, Guangzhou, China) was double-distilled using a quartz distiller under sub-boiling conditions.

Ultrapure water: Distilled water was purified by Milli-Q™ 185 PLUS system (Millipore S.A., France).

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The grades and manufacturers of the single-element standard solutions are listed in Table II.

### TABLE II
**Single-Element Standard Solutions**

<table>
<thead>
<tr>
<th>Element</th>
<th>Grades</th>
<th>Manuf.</th>
</tr>
</thead>
<tbody>
<tr>
<td>As, Cd, Cr, Hg, Ni, Pb, Zn</td>
<td>GBW</td>
<td>NRCCRM&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Co, Mn, Mo, Sc, V</td>
<td>GBW(E)</td>
<td>NRCCRM</td>
</tr>
<tr>
<td>Sn</td>
<td>BW</td>
<td>NRCCRM</td>
</tr>
<tr>
<td>Pd, Re, Rh, Tl</td>
<td>GSBG</td>
<td>CNISATC&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Standard grades of China.
<sup>b</sup> National Research Center for Certified Reference Materials, Beijing, China.
<sup>c</sup> China National Iron & Steel Analysis Test Center, Beijing, China.

### Method

Internal standards were used in the quantitative analysis to correct for instrumental drift. Rhodium was used as the internal standard for the medium mass elements (V, Cr, Mn, Co, Ni, Zn, As, Se, Mo, Pd, Cd, and Sn); Re was used as the internal standard for the high-mass elements (Hg, Tl, and Pb). The concentrations of internal standard elements in blank, sample, and calibration solutions were 1 ng/mL.

Calibration solutions were prepared by mixing standard solutions of single elements, which were diluted by 1% HNO₃ to three levels of concentration by weight. The concentration levels used for V, Cr, Co, Pd, Sn, Hg, and Tl were 0.1, 1.0, and 10 ng/mL; for Ni, As, Se, Mo, Cd, and Pb 0.5, 5.0, and 50 ng/mL; and for Mn and Zn 3.0, 30, and 300 ng/mL.

The isotopes measured are listed in Table III and the equations used for interference correction are listed in Table IV.

For solid samples, including edible oil, 0.5-g samples were accurately weighed into a Teflon® vessel for digestion in a microwave oven and 3 mL HNO₃ was added, and the vessel sealed with the cap. The sample was digested in the microwave oven at 160 W for 20 minutes and then at 320 W for 20 minutes. The cooled digest was filtered and removed into a 50-mL glass comparison tube with scale. The wall of the Teflon vessel was rinsed with a little water and the rinse water filtered into the comparison tube. This solution was spiked with 1 mL internal standard solution containing 50 ng/mL each of Rh and Re, and then diluted up to 50 mL volume with H₂O. Laboratory blanks were prepared in the same manner as the samples.

For liquid samples, a 5-g sample was weighed accurately into a 50-mL glass tube and 5 mL H₂O and 3 mL HNO₃ were added, then shaken to mix. The sample tube was put into a waterbath and the sample digested at about 100°C for two hours. The cooled digest was filtered and removed into a 50-mL glass comparison tube with scale. The wall of the sample tube was rinsed with a little water and the rinse water filtered into the comparison tube. The sample was spiked with a 1-mL internal standard solution containing 50 ng/mL each of Rh and Re and then diluted to 50 mL volume with H₂O. The blank sample was prepared in the same way.

For water samples, 0.5 mL HNO₃ was put into a 50-mL glass comparison tube including 1 mL internal standard solution containing 50 ng/mL each of Rh and Re, and then made up to 50-mL volume with H₂O. The blank sample was prepared with ultrapure water in the same way.

All containers were soaked in nitric acid (A.R.) for two days and in 10% suprapure nitric acid for one day, washed in ultrapure water, and dried before use.

### TABLE III
**Measuring Isotopes, Correlation Coefficient (CC), and Relative Standard Deviation (RSD)**

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass (amu)</th>
<th>CC</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>51</td>
<td>1</td>
<td>2.1</td>
</tr>
<tr>
<td>Cr</td>
<td>53</td>
<td>0.99999</td>
<td>4.4</td>
</tr>
<tr>
<td>Mn</td>
<td>55</td>
<td>0.99999</td>
<td>0.5</td>
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<tr>
<td>Co</td>
<td>59</td>
<td>0.99995</td>
<td>0.4</td>
</tr>
<tr>
<td>Ni</td>
<td>60</td>
<td>0.99994</td>
<td>0.4</td>
</tr>
<tr>
<td>Zn</td>
<td>66</td>
<td>0.99999</td>
<td>0.8</td>
</tr>
<tr>
<td>As</td>
<td>75</td>
<td>0.99999</td>
<td>1.3</td>
</tr>
<tr>
<td>Se</td>
<td>82</td>
<td>0.99999</td>
<td>1.3</td>
</tr>
<tr>
<td>Mo</td>
<td>98</td>
<td>0.99999</td>
<td>0.4</td>
</tr>
<tr>
<td>Pd</td>
<td>104</td>
<td>0.99999</td>
<td>2.3</td>
</tr>
<tr>
<td>Cd</td>
<td>111</td>
<td>0.99999</td>
<td>0.7</td>
</tr>
<tr>
<td>Sn</td>
<td>120</td>
<td>0.99999</td>
<td>0.8</td>
</tr>
<tr>
<td>Hg</td>
<td>202</td>
<td>0.99997</td>
<td>2.8</td>
</tr>
<tr>
<td>Tl</td>
<td>205</td>
<td>0.99999</td>
<td>0.7</td>
</tr>
<tr>
<td>Pb</td>
<td>208</td>
<td>0.99993</td>
<td>0.6</td>
</tr>
<tr>
<td>Rh</td>
<td>103</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re</td>
<td>185</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE IV
**Equations of Interference Correction**

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass (amu)</th>
<th>Correction equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>75</td>
<td>-3.127 * Se 77 + 2.73 * Se 82</td>
</tr>
<tr>
<td>Se</td>
<td>82</td>
<td>-1.008696 * Kr 83</td>
</tr>
<tr>
<td>Mo</td>
<td>98</td>
<td>-0.110588 * Ru 101</td>
</tr>
<tr>
<td>Pd</td>
<td>104</td>
<td>-1.10 * Ru 101</td>
</tr>
<tr>
<td>Cd</td>
<td>111</td>
<td>-1.073 * MoO 108 + 0.764 * Pd 106 + 0.336 * Pd 105</td>
</tr>
<tr>
<td>Sn</td>
<td>120</td>
<td>-0.013447 * Te 125</td>
</tr>
</tbody>
</table>
Sample homogeneity is a major source of error since smaller sample weights are required due to dissolved solids limitation in ICP-MS. In comparing the analysis of reference materials, the systematic deviation between test techniques is also an important factor because the certified values of reference materials made in China were determined by techniques other than ICP-MS. As concentrations of toxic elements in normal foods are all at trace levels, clean containers and tools are necessary for preventing from accidental contamination. However, an accidental error from contamination of a food sample or from a sample introduction system is usually difficult to prove for specific element(s). In order to ensure accurate results, it is best to use new calibration solutions.

CONCLUSION
The results of this study show that ICP-MS can be used effectively for the simultaneous determination of toxic elements at trace levels in various food materials. It was found that the identical calibration curve could be applied to the analysis using the ELAN 6000 ICP-MS when...

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**TABLE V**

Analytical Results for Reference Materialsa (ng/g)

<table>
<thead>
<tr>
<th>Element</th>
<th>Rice powder</th>
<th>Pork liver</th>
<th>Mussels</th>
<th>Milk powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>9.8 Ref.</td>
<td>8.32 Found</td>
<td>10.2 Ref.</td>
<td>0.28 Ref.</td>
</tr>
<tr>
<td>Co</td>
<td>9.5 Found</td>
<td>14.8 Found</td>
<td>138 Ref.</td>
<td>6.1 Ref.</td>
</tr>
<tr>
<td>Ni</td>
<td>1.03 0.90</td>
<td>10.3 0.90</td>
<td>46.8 43.0</td>
<td>0.31 0.34</td>
</tr>
<tr>
<td>Zn</td>
<td>0.051 0.051</td>
<td>0.044 0.066</td>
<td>0.22 0.41</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.045 0.050</td>
<td>0.067 0.077</td>
<td>4.5 4.0</td>
<td></td>
</tr>
<tr>
<td>Se</td>
<td>0.54 0.59</td>
<td>0.067 0.073</td>
<td>0.034 0.012</td>
<td></td>
</tr>
</tbody>
</table>

a Prepared by NRCCRM.

**TABLE VI**

Results of Recovery Test (%)

<table>
<thead>
<tr>
<th>Element</th>
<th>Spike (ppm)</th>
<th>Fine flour</th>
<th>Milk powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>0.10</td>
<td>94</td>
<td>103</td>
</tr>
<tr>
<td>Cr</td>
<td>0.10</td>
<td>169</td>
<td>147</td>
</tr>
<tr>
<td>Mn</td>
<td>3.0</td>
<td>88</td>
<td>85</td>
</tr>
<tr>
<td>Co</td>
<td>0.10</td>
<td>218</td>
<td>111</td>
</tr>
<tr>
<td>Ni</td>
<td>0.50</td>
<td>67</td>
<td>110</td>
</tr>
<tr>
<td>Zn</td>
<td>3.0</td>
<td>105</td>
<td>155</td>
</tr>
<tr>
<td>As</td>
<td>0.50</td>
<td>159</td>
<td>155</td>
</tr>
<tr>
<td>Se</td>
<td>0.50</td>
<td>156</td>
<td>149</td>
</tr>
<tr>
<td>Mo</td>
<td>0.50</td>
<td>100</td>
<td>105</td>
</tr>
<tr>
<td>Pd</td>
<td>0.10</td>
<td>79</td>
<td>99</td>
</tr>
<tr>
<td>Cd</td>
<td>0.50</td>
<td>97</td>
<td>99</td>
</tr>
<tr>
<td>Sn</td>
<td>0.10</td>
<td>95</td>
<td>125</td>
</tr>
<tr>
<td>Hg</td>
<td>0.10</td>
<td>73</td>
<td>137</td>
</tr>
<tr>
<td>Tl</td>
<td>0.10</td>
<td>100</td>
<td>95</td>
</tr>
<tr>
<td>Pb</td>
<td>0.50</td>
<td>176</td>
<td>115</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSION**

Calibration Curve
Calibration solutions were run using the operating conditions mentioned above. The correlation coefficient (CC) of the calibration curves for the elements V, Cr, Mn, Co, Ni, Zn, As, Se, Mo, Cd, Sn, Hg, Ti, and Pb are listed in Table III.

Accuracy
Table V lists the analytical results for the reference materials of rice powder, pork liver, mussels, and milk powder.

Table VI lists the spike recoveries obtained for all elements when a known amount of standard solution was added to the samples.

Precision
The relative standard deviations (RSD) obtained from 10 replicate measurements of a sample solution are also listed in Table III.

Sample Analysis
The concentrations of the toxic elements in different foods, wine, and water were determined and are summarized in Table VII.

Memory Effects
Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, and from the residue of sample material in the sample introduction system including ICP torch, spray chamber, nebulizer, pump tubing, and sample capillary tubing. The site where these effects occur is element-dependent and can be minimized by flushing the system with an appropriate rinse solution between samples. In the determination of mercury, severe memory effects may be encountered. The document for use of the U.S. EPA Method 200.8 (14) reports that a rinse solution containing 2% nitric acid and 100 ng/mL gold could effectively rinse 5 ng/mL mercury in approximately two minutes. The authors compared the rinse-out effects of two rinse solutions: 1% HNO₃ and 1% HNO₃ with 100 ng/mL Au. Washout was tested after rinsing 5 ng/mL Hg for 25 minutes and 10 ng/mL Hg for five minutes, respectively. The rinse-out process for 5 ng/mL Hg is shown in Figure 1. The rinse-out process for 10 ng/mL Hg is not shown but was similar to Figure 1. From this data it was concluded that the timed rinsing system with a 1% HNO₃ solution for about five minutes is sufficient for general food samples.
the same operating conditions were used over a period of 1–3 weeks. It was not necessary to perform calibration every day as long as the intensity of the internal standard remained close to the previously measured intensities.

The precision/repeatability of ICP-MS has advanced greatly in comparison to other inorganic mass spectrometry techniques such as spark source mass spectrometry and secondary ion mass spectrometry (15,16).

Received March 12, 1997.

REFERENCES


### TABLE VII

Analytical Results for Various Food Materials (ppb)

<table>
<thead>
<tr>
<th>City</th>
<th>Element</th>
<th>Belt-</th>
<th>Beef</th>
<th>Chicken</th>
<th>Pork</th>
<th>Mussels</th>
<th>Rice flour</th>
<th>Corn</th>
<th>Celery</th>
<th>Shad</th>
<th>Raw</th>
<th>Tea</th>
<th>Orange</th>
<th>Peanut</th>
<th>Red</th>
<th>Spring</th>
<th>Tap</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>fish</td>
<td></td>
<td>stomach</td>
<td>liver</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>V</td>
<td>53</td>
<td>19</td>
<td>80</td>
<td>52</td>
<td>650</td>
<td>26</td>
<td></td>
<td>46</td>
<td>5</td>
<td>27</td>
<td>540</td>
<td>5</td>
<td>1</td>
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<td>0.9</td>
<td></td>
</tr>
<tr>
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<td>200</td>
<td>210</td>
<td>390</td>
<td>220</td>
<td>840</td>
<td>450</td>
<td>630</td>
<td>310</td>
<td>57</td>
<td>160</td>
<td>1700</td>
<td>110</td>
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<td>42</td>
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<td>0.8</td>
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<tr>
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<td>300</td>
<td>130</td>
<td>820</td>
<td>2800</td>
<td>7000</td>
<td>9800</td>
<td>2600</td>
<td>2400</td>
<td>1800</td>
<td>2100</td>
<td>670</td>
<td>320</td>
<td>710</td>
<td>860</td>
<td>6</td>
<td>100</td>
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<tr>
<td>Co</td>
<td>2</td>
<td>5</td>
<td>15</td>
<td>29</td>
<td>390</td>
<td>67</td>
<td>38</td>
<td>160</td>
<td>9</td>
<td>55</td>
<td>270</td>
<td>10</td>
<td>29</td>
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<tr>
<td>Ni</td>
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<td>110</td>
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<td>3</td>
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<td>0.5</td>
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</tr>
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<td>3</td>
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<tr>
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<td>6</td>
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<td>490</td>
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<td>48</td>
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Fig. 1. Residual memory effects for Hg washout as a function of rinse solution.