Improved measurement of iodine in food samples using inductively coupled plasma isotope dilution mass spectrometry

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A new ICP-MS method for the determination of iodine in food samples is presented. The method makes use of a new miniature cyclonic spray chamber and a concentric glass nebulizer that is designed for low sample uptakes and is operated in a self-aspirating mode. As a consequence the wash-out was accelerated over conventional systems. This configuration allows the direct determination of iodine in mineralized solutions following digestion with nitric acid only. No strong oxidizing reagents such as perchloric acid or lengthy sample preparation were necessary to alter the chemical form of potentially volatile species. The isotope dilution technique using the long-lived isotope \(^{127}\)I was applied to obtain freedom from matrix effects. The present study reports on results for total iodine in selected nutritional and biological reference materials and makes a comparison with instrumental neutron activation analysis.

Introduction

Dietary iodine deficiency causes abnormal biochemical thyroid function. Although the importance of iodine for preventing endemic goitre has been recognized for more than a century it is only during the past 30 years that a wide range of subtle harmful effects of iodine deficiency have been described. Dietary iodine deficiency can influence the fetal neurological development during pregnancy but the effects of iodine deficiency disorders (IDD) occur at all stages of human growth, from the fetus through to adulthood. In a recent study thyroid dysfunction was associated with adverse cardiovascular health. A decrease of the iodine status has been registered in several countries for the past few years and yet direct measurements of dietary iodine have been rare. In human nutrition studies, the recommended method for assessing the iodine status within a group of individuals is to measure the iodine excretion in urine. However, iodine data of food are important to monitor possible modifications of its content and hence serve as a basis for dietary recommendations.

The determination of iodine in food has been a difficult analytical problem for many years and inconsistent results have been obtained in interlaboratory studies. For the determination of low concentrations sensitive analytical methods with a low risk of contamination are necessary. From this point of view neutron activation analysis (NAA) is a superior technique. However, for a long time the catalytic method based on the Sandell-Kolthoff reaction has been preferred for iodine determinations in biological materials. Today, ICP-MS has proved to be very useful to determine iodine in biological samples. The full exploitation of this technique, however, requires careful optimization of the analytical parameters.

The determination of iodine in nutritional samples introduces additional complications when solid samples are being digested with acid. Poor stability and memory effects occur at low pH in the presence of iodide and are attributed to the formation of volatile species such as HI and I\(_2\). Therefore, sample preparation or decomposition are critical steps in iodine analysis. Nitric acid digestions were normally combined with perchloric acid as a strong oxidizing reagent to convert the volatile iodine species into non-volatile species. However, perchloric acid is a hazardous reagent and the oxidized solutions may not be stable after dilution. An increasingly popular alternative approach to acid digestion is alkaline extraction with tetramethylammonium hydroxide (TMAH). The measurement of iodine in alkaline solution suppresses the formation of volatile species; however, incomplete extractions were observed for certain sample types. Low recoveries reflect insoluble forms of iodine present, i.e. covalently bonded, and thus require mineralization before analysis. Both reagents, perchloric acid as well as TMAH, normally contain considerable amounts of iodine as a contaminant.

In view of the restrictions of these approaches a new method to measure low concentrations of iodine in food or food-related samples accurately and reliably was developed. Furthermore, it involved a nitric acid digestion step without the use of additional oxidizing reagents. The combination of pneumatic nebulizer and spray chamber is primarily used in ICP-MS; however, selective evaporation of volatile iodine species may cause non-quantitative recoveries and severe sample carry-over effects in the ICP introduction system. In this study a reduced size cyclonic spray chamber that exhibits fewer sample-aerosol interactions was used to overcome such difficulties. Reducing spray chamber volume and surface has the advantage of eliminating sample carry-over effects; however, this improvement is optimal when the total amount of sample nebulized per time unit is also reduced. To this end a new class of low-uptake concentric nebulizers was employed in combination with the reduced size spray chamber. This approach is mid-way between conventional sample introduction systems, i.e. with a Scott-type double pass spray chamber, and a direct injection nebulizer (DIN). The DIN would be a possible alternative as its operation requires no spray chamber, but is not straightforward to use on a routine basis.

In addition, the isotope dilution analysis (IDA) technique has been used as it is an accurate technique that is independent of matrix effects. IDA can be applied to all elements with at least two isotopes, and also to monoisotopic elements such as iodine provided that a long-lived artificial isotope exists. Losses of the element during preparation procedures, i.e. mineralization, have
no influence on the result of the analysis. Previous ICP-MS applications of iodine IDA were carried out at alkaline pH values,\textsuperscript{6,14} introducing elemental iodine via the gas phase into the plasma\textsuperscript{17} or with an oxidizing agent.\textsuperscript{10} The present study reports on the application of the proposed method to selected nutritional or biological reference materials. Results of total diet sample determinations were compared with those obtained by NAA to reveal a possible bias.

**Experimental**

**Instrumentation**

An Elan 5000 ICP-MS instrument (Perkin-Elmer SCIEX, Norwalk, CT, USA) was equipped with a standard torch, nickel cones and a micro-autosampler (CETAC ASX-100, Omaha, NE, USA). The original detector was replaced by a discrete-dynode, Type ETP AF570 (ETP Scientific, Auburn, MA, USA). The autosampler is designed for use with sample introduction systems requiring low flow rates of the sample solutions. A sample rack that holds 24 vessels (1–3 ml) was used. A PEEK capillary (id 0.05 cm, Upchurch Scientific, Oak Harbor, WA, USA) was directly connected to the PTFE tubing of the MicroMist low-uptake nebulizer (Glass Expansion, Hawthorn, Australia). The nebulizer and spray chamber used for this study are described in more detail below. The plasma conditions and measurement parameters are listed in Table \ref{table:1}.

**Aerosol generation and introduction system**

The new devices were two aerosol-generation components developed by Glass Expansion P/L., Australia, for the improvement of ICP sample introduction. A spray chamber of reduced volume was used, the Cinnabar mini-cyclonic spray chamber, and a MicroMist low-uptake nebulizer. Fig. 1 shows these components. The Glass Expansion MicroMist is a concentric glass pneumatic nebulizer with a narrow, conical sample capillary that is machined from a cylinder of solid borosilicate glass. The particular type used in this study was the AR30-1-F02, which has an argon flow of 1.0 l min$^{-1}$ and an aspirated uptake of 200 $\mu$l min$^{-1}$ at an applied pressure of 3 bar. The MicroMist was operated with aspirated uptake to avoid a peristaltic pump tube that could itself be a source of iodine contamination by absorption and to avoid signal instabilities caused by mechanical pumping.

The Cinnabar is a mini-cyclonic spray chamber made of borosilicate glass. Its chamber internal diameter and height are 38 and 32 mm, respectively, and its volume is 20 ml. For the sample introduction conditions used in this study the mass-flow ratio of tertiary aerosol to sample uptake is approximately 30% and matrix effects are reduced five-fold compared with the standard Elan sample introduction system.\textsuperscript{18} This last-mentioned result is thought to be because of reduced droplet collisional and coalescence effects.\textsuperscript{19}

For comparison a slurry concentric nebulizer (Glass Expansion P/L.) made for higher sample flow rates (approximately 3 ml min$^{-1}$) was fitted to a Scott-type spray chamber (Perkin-Elmer) made from Ryton (100 cm$^3$) and was also used.

**Chemicals**

Water was purified and de-ionized (18 M$\Omega$) using the cartridge system Easy Pure LF (Barnstead, Dubuque, IA, USA). Suprapur nitric acid was obtained from Merck (Darmstadt, Germany). The iodine concentration of these reagents was below 0.5 ng ml$^{-1}$.

The NIST SRM 4949C $^{129}$I radioactivity standard is suitable for IDA. $^{129}$I is a low-energy $\beta$ emitting isotope of iodine with a half-life of 1.57 $\times$ 10$^7$ years. The activity of the solution was certified at 3451 $\pm$ 22 Bq g$^{-1}$ which is equal to a concentration of 528 mg l$^{-1}$. The concentration of $^{127}$I was not certified; however, an atom fraction of 14% $^{127}$I and 86% $^{129}$I, corresponding to a $^{129}$I/$^{127}$I ratio of 6.1 $\pm$ 0.06% (RSD 1%), was measured in another study. In general, the natural abundance of $^{129}$I is negligible although transfer into the food chain was observed following nuclear accidents. In environmental and biological samples, $^{129}$I/$^{127}$I ratios from 10$^{-10}$ to 10$^{-6}$ were measured, which are of no analytical concern.\textsuperscript{22}

**Samples**

Several certified reference materials were obtained from the National Institute of Standards and Technology (NIST) and the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>ICP-MS operating conditions and measurement parameters</th>
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</thead>
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<tr>
<td>Rf power/W</td>
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</tr>
<tr>
<td>Argon flow rate/l min$^{-1}$:</td>
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</tr>
<tr>
<td>nebulizer</td>
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<td>Replicates</td>
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</tr>
<tr>
<td>Wash time/s</td>
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</tr>
</tbody>
</table>

Fig. 1 Cinnabar spray chamber and MicroMist low-uptake nebulizer with a metric scale (cm).
European Community Bureau of Reference (BCR). Total diet samples were obtained from a former survey of the Swiss diet (January 1983). Each diet was sampled, homogenized and dried by freeze-drying. Inhomogeneity was less than 5% for a sample of 100 mg. In general, no loss of various iodine species occurs during freeze-drying. The dried samples were stored in a deep freezer (−20 °C) until the time of the ICP-MS measurement. It was assumed that the samples were stable under these conditions with reference to iodine although there are no reference data on long-term storage. A preceding iodine determination in the total diet samples was carried out by instrumental neutron activation analysis (NAA) after activation with epithermal neutrons. Details of the NAA procedure were described elsewhere.

Sample preparation and digestion

Particular attention was given to the sample pre-treatment to avoid possible loss of iodine at initial stages. A mass of 100−200 mg of dried sample was weighed directly into 15 ml quartz vessels and 250 μl of water were added. According to the expected content in the sample a definite volume of a solution of 1 μg ml⁻¹ equal to a mass of 10−600 ng ¹²⁹I was dispensed onto the suspension and mixed with a circular motion. A 750 μl volume of nitric acid was added and each vessel was sealed with strips of PTFE tape and closed with a lid immediately. The vessels were placed in the high pressure asher–autoclave, HPA (Kürner, Rosenheim, Germany).

The autoclave holds 21 vessels for digestion. It was closed and filled with nitrogen at an initial pressure of 100 bar. The external autoclave pressure was restricted to 130 bar by a release valve. The following heating program was used for nitric acid digestion: 80−110 °C over 30 min and then 90 min at 230 °C. As the vessels were heated the counterpressure still exceeded the reaction pressure, thus keeping the lids closed. Once the temperature program was finished the autoclave cooled down to below 30 °C, leaving a residual pressure in the vessels. After the nitrogen had been released slowly from the autoclave, the vessels were removed and opened. The solutions were diluted with water to a volume of 3 ml.

Results and discussion

Blank values and detection limit

The blanks were determined by the same analytical procedure as the sample. No elevated blank levels at m/z 127 (stable iodine) were observed, contrary to other studies. The signal intensities corresponded to the basic instrumental noise. Blank variations introduced by memory effects, such as from contamination, were not observed. At m/z 129 the intensities were at least a factor of 2 higher. This was attributed to interference by ¹²⁹Xe. Xenon occurs as a trace contaminant in the plasma gas argon.

In IDA the detection limit (D_L) depends on the isotope ratio of the spike. The D_L was calculated based on the regression line, therefore, a series of the ¹²⁹I spike solutions at 10 ng ml⁻¹ with ¹²⁷I amounts at the lower end of the concentration domain were added and the resulting ¹²⁷I/¹²⁹I ratios were measured. Fig. 2 shows the regression line with its 95% confidence limits through the ¹²⁷I/¹²⁹I ratios versus the iodine concentrations and the location of the D_L on the x-axis. The D_L is defined as the upper limit of the concentration confidence interval for the lowest concentration whose ratio can be distinguished from the ratio of the added spike. A D_L of 0.6 ng ml⁻¹ was estimated that corresponded to a relative D_L of 5−10 ng g⁻¹ in a biological sample, depending on the mass and dilution of the digested sample.

Interferences

Isotope dilution methods generally correct for non-spectroscopic matrix effects, however, isobaric overlaps or molecular ions can affect the ion intensity of an iodine isotope and therefore disturb the ¹²⁹I/¹²⁷I ratio. In this connection, the isotope ¹²⁹Xe is a problem and its ionization could be affected by the matrix. For the subsequent determinations of iodine in certified reference materials and the total diet samples the non-interfered ¹³¹I was monitored as well, however, no significant changes of its signal were observed throughout the measurements. The contribution of ¹²⁹Xe at m/z 129 was therefore eliminated by subtraction of the intensities measured in blank solutions.

In addition, some concomitant elements could produce molecular ion interferences. The most significant molecular ions are the molecular oxides of atomic iodine. A preliminary assessment was therefore given to Cd, which is likely to form interfering ¹¹¹CdO⁺ or ¹¹³CdO⁺. The measurement of Cd at 100 μg ml⁻¹ in nitric acid (6%) resulted in oxide interferences at m/z 127 and 129 that correspond to iodine concentrations of 0.4 and 0.3 ng ml⁻¹, respectively. Such Cd concentrations, however, are irrelevant in food sample solutions. High Cd concentrations were found in mushrooms for example. If such samples containing Cd at 50 μg g⁻¹ (dry matter) were digested according to the protocol in this study, it would yield about 3 μg ml⁻¹ in the resulting sample solution only.

Isotope dilution analysis

To attain the smallest uncertainty on a quantitative determination by isotope dilution analysis a proper choice of sample-to-spike ratio has to be made. ¹²⁹I/¹²⁷I ratios between 1 and 3 were measured in the spiked sample solutions under study. For example, in the certified reference materials Pine Needles (0.09 μg g⁻¹ iodine) and Whole Egg (2.4 μg g⁻¹ iodine), ratios of 2.3 ± 0.1 (RSD 4.3%) and 1.54 ± 0.01 (RSD 0.8%), respectively, were measured. The propagated uncertainty was calculated for the system of a stable isotope using an artificial isotope as spike. The relative uncertainties for the iodine concentration in the gravimetrically diluted spike solution and its ¹²⁹I/¹²⁷I isotope ratio were 0.6 and 1.0%, respectively. These data were taken either from the NIST certificate or from other assays, ¹²⁹I/¹²⁷I ratios from 1 to 3 with values for the uncertainties in these ratios taken to be either 4.3 or 0.8% result in estimated uncertainties on the iodine determination of 5−9 or 1−2%, respectively. If the spike is accurately assayed the precision with which a ratio in the sample solution can be measured

Fig. 2 Lowest detectable changes in the ¹²⁷I/¹²⁹I ratio as a result of small amounts of ¹²⁷I added to the NIST SRM 4949C ¹²⁹I standard solution (10 ng ml⁻¹). The 95% confidence limits of the regression line map the detection limit on the concentration axis.

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determines the uncertainty in the final result. Furthermore, optimal spiking conditions are achieved for ratios close to unity.

For accurate isotope ratio measurements, both the detector dead time and the mass discrimination have to be corrected for. The detector dead time was estimated as demonstrated by Vanhaecke et al.\textsuperscript{31} Using solutions of the NIST 4949C standard a dead time of about 40 ns was obtained and the correction was made accordingly. For the Elan 5000 instrument the detector dead time was strongly dependent on the mass. Mass discrimination effects are common in isotope ratio measurements using quadrupole based ICP-MS instruments. Several parameters of the instrument contribute to this phenomenon, mainly nebulizer gas flow and ion optics lens potentials. The lens voltages were set to achieve a $^{129}\text{I}/^{127}\text{I}$ ratio that is biased by less than 5% using a 10 ng ml$^{-1}$ solution of the NIST SRM 4949C and the systematic error was corrected by a factor that was calculated from the ratio of the true and the measured isotope ratio, e.g. 1.030 ± 0.001.

**Wash-out characteristics**

The time required for a signal to fall back to its initial value is an important analytical parameter as it serves as a reference point for changing samples and thus determines the rate of analysis. Principal factors that determine the signal decay time for potentially volatile analytes such as iodine in an acidic solution are the volume and the surface area of a spray chamber. The relative performance of the Cinnabar was assessed by comparison with a conventional Scott-type spray chamber. Nebulizer design can affect the wash-out time as well; therefore, similar concentric flow nebulizers were used for a comparison. The MicroMist low-uptake nebulizer was used with the Cinnabar and a slurry nebulizer for higher sample uptakes was used with the Scott spray chamber. Both nebulizers were operated in a self-aspirating mode at an identical aerosol argon flow rate of 1 l min$^{-2}$, which produced nearly the same maximum iodine signal intensity for both systems. The sample uptakes were set by varying the sample tube dimensions, to maximum iodine signal intensity for both systems. The sample uptakes were smoothed to conceal short-term fluctuations and make the curve indicated the presence of secondary clean-out processes.

Fig. 3 shows various wash-out profiles for iodide (I$^-$), elemental iodine (I$_2$) and iodate (IO$_3^-$) solutions in 6% nitric acid at equal concentration levels of 50 ng ml$^{-1}$. The signals were smoothed to conceal short-term fluctuations and make the profiles more apparent. Evidently, IO$_3^-$ is the ideal species for iodine measurements as the return of the signal to its initial baseline value is fast and independent of the spray chamber type. In contrast, it was impracticable to measure I$^-$ using the Scott spray chamber. Within the measurement time the signal did not arrive at a steady-state before the wash-out was initiated and the rinsing was extremely slow as more than 30 min were required for the signal to drift down to its initial value.

The Cinnabar spray chamber proved to be useful for the determination of all iodine species. The signals differed somewhat in profile and intensity, but even the I$^-$ determination of all iodine species. The signals differed required for the signal to drift down to its initial value. For the Elan 5000 instrument the detector dead time was strongly dependent on the mass. Mass discrimination effects are common in isotope ratio measurements using quadrupole based ICP-MS instruments. Several parameters of the instrument contribute to this phenomenon, mainly nebulizer gas flow and ion optics lens potentials. The lens voltages were set to achieve a $^{129}\text{I}/^{127}\text{I}$ ratio that is biased by less than 5% using a 10 ng ml$^{-1}$ solution of the NIST SRM 4949C and the systematic error was corrected by a factor that was calculated from the ratio of the true and the measured isotope ratio, e.g. 1.030 ± 0.001.

In general, the wash-out time of the various species increased in the following order: IO$_3^-$ $<$ I$_2$ $<$ I$^-$. This behaviour is emphasized if the spray chamber is more voluminous and its surface is larger as is the case with the Scott-type. As a consequence, when conventional sample introduction devices are used even the measurement of IO$_3^-$ may lead to erroneous results if it is unstable and conversion to other species occurs during the process of analysis.\textsuperscript{11,13} Another important aspect was long-term iodine memory. Such memory effects can lead to an isotope ratio different from the true value. Typically, when the Scott spray chamber was used, the background $^{127}\text{I}$ count rate was 800–1200 counts s$^{-1}$ compared with 150–200 counts s$^{-1}$ with the Cinnabar. The Cinnabar system exhibited lower memory effects, a feature attributable to the small surface and the favourable shape. The cyclonic form prevents sample solution building up around the spray chamber and possibly being re-nebulized. In addition, the spray chamber was slightly tilted to ensure that all droplets that are thrown against the chamber walls run away from the tangential nebulizer inlet and leave via the central drain tube at the base.

**Acid digestion**

During an oxidizing acidic digestion procedure in combination with perchloric acid or hydrogen peroxide, IO$_3^-$ is formed as the predominant species.\textsuperscript{32} In this study no additional reagents were added to enhance the oxidizing strength of the nitric acid. Under these specific conditions nitric acid reaction products such as NO generated during the oxidation process of organic matter remain dissolved in the solution and are thus capable of
 reducing strong oxidants, e.g. selenate. Likewise, IO$_3^-$ can be reduced if it was initially present.

Preliminary tests using the Scott spray chamber showed that solutions derived from the digestion of food samples with nitric acid yielded wash-out profiles similar to those seen with the I$^{-}$ standard in Fig. 3b1. It was therefore concluded that the predominant iodine species in the solutions after nitric acid digestion was I$^{-}$. The addition of the $^{129}$I spike before the acid digestion ensures equilibration between sample and spike iodine after the process has finished. Thus, species-dependent signal intensities would affect both isotopes equally.

The closed vessel high-pressure asher prevented losses during the digestion procedure. Possible losses of iodine after venting the vessels at a slightly elevated pressure were compensated by proportional losses of the $^{129}$I isotope.

### Determination of iodine in food-related certified reference materials

The performance of the analytical method was tested using certified reference materials (CRM) that covered a wide range of food or food-related sample types and contained iodine from 0.006 to 3.38 µg g$^{-1}$ (dry matter). The results of at least four independent analyses are summarized in Table 2. The obtained values agree closely with the certified or reported values at the 95% confidence interval (CI). Some of the CI of the measured values quoted in Table 2 do not compare with the CI of the reference material as the latter includes also uncertainties from other methods inherent in the certification of the material, i.e. the NIST RM 8415. Even materials with low iodine concentrations below 0.1 µg g$^{-1}$ yielded good results, a range of concentration in which inconsistent results among other methods were reported. It should be noted that although the measured iodine concentration of the Wheat Flour agrees well with the certified value it is close to the detection limit and reflects the order of magnitude only. The precision (RSD) of the obtained value is 1.8—5%.

### Comparison of methods

The relative linear relationship between the ICP-MS method and a purely instrumental NAA reference method was assessed through the linear model: $C_{\text{ICP}} = a + bC_{\text{NAA}}$. The ordinary least squares linear regression line was calculated with the measured ($C_{\text{ICP}}$) and the reference iodine concentration values ($C_{\text{NAA}}$) of a series of nine total diet samples containing iodine in the range 0.3–1.8 µg g$^{-1}$ (dry matter). The hypothesis $a = 0$ and $b = 1$ that indicates absence of systematic errors was tested. In calculating the regression line one of the basic assumptions was violated, i.e. the error of the predictor variable ($C_{\text{NAA}}$) was assumed.

### Conclusion

The determination of iodine in a nitric acid matrix by ICP-MS is improved significantly when the components of the sample introduction system are chosen so that the total amount of sample consumed and being processed is reduced to an absolute minimum. In contrast to the DIN approach, which is normally used to achieve this end, the approach used in this work is based on components that are similar in conception to conventional aqueous sample introduction components. This approach therefore offers the advantages of greater simplicity, lower cost and easy automation.

### Table 2

<table>
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<th>Sample</th>
<th>n</th>
<th>Obtained value</th>
<th>RSD (%)</th>
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<td>Non-Fat Milk Powder, NIST SRM 1549</td>
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<td>2.03 ± 0.12</td>
<td>4</td>
<td>1.97 ± 0.46</td>
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<tr>
<td>Total Diet, NIST SRM 1548</td>
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*Mean and 95% confidence interval for n independent determinations.*

Fig. 4 Results of iodine ICP-MS determinations in total diet samples plotted versus reference values obtained by epithermal NAA ($r = 0.992$).
greater ease of use as no additional analytical steps such as extraction, filtration and chemical modifications such as oxidation, increasing pH values or generation of gas phase iodine, are required.

Acknowledgements

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References