Talanta 79 (2009) 235–242

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Trace iodine quantitation in biological samples by mass spectrometric methods The optimum internal standard

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ARTICLE INFO

Article history:
Received 26 January 2009
Received in revised form 13 March 2009
Accepted 16 March 2009
Available online 26 March 2009

Keywords:
Iodine
ICP-MS
ESI-MS
Iodine-129
Isotope dilution mass spectrometry

ABSTRACT

Accurate quantitation of iodine in biological samples is essential for studies of nutrition and medicine, as well as for epidemiological studies for monitoring intake of this essential nutrient. Despite the importance of accurate measurement, a standardized method for iodine analysis of biological samples is yet to be established. We have evaluated the effectiveness of ^{72}Ge, ^{115}In, and ^{129}I as internal standards for measurement of iodine in milk and urine samples by induction coupled plasma mass spectrometry (ICP-MS) and of $^{35}Cl^{18}O_4{}^-$, $^{129}I^-$, and 2-chlorobenzenesulfonate (2-CBS) as internal standards for ion chromatography-tandem mass spectrometry (IC-MS/MS). We found recovery of iodine to be markedly low when IC-MS/MS was used without an internal standard. Percent recovery was similarly low using $^{35}Cl^{18}O_4$ as an internal standard for milk and unpredictable when used for urine. 2-Chlorobenzebenzenesulfonate provided accurate recovery of iodine from milk, but overestimated iodine in urine samples by as much as a factor of 2. Percent recovery of iodine from milk and urine using ICP-MS without an internal standard was ~120%. Use of ^{115}In predicted approximately 60% of known values for both milk and urine samples. ^{72}Ge provided reasonable and consistent percent recovery for iodine in milk samples (~108%) but resulted in ~80% recovery of iodine from urine. Use of ^{129}I as an internal standard resulted in excellent recovery of iodine from both milk and urine samples using either IC-MS/MS and ICP-MS.

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1. Introduction

During the present decade there has been great interest on perchlorate in the environment [1,2]. Although unreactive at physiological pH, perchlorate is a powerful competitive inhibitor for the transport of the essential iodide ion via the sodium-iodide symporter [3,4] and excessive intake of perchlorate may result in iodine deficiency. Obviously, this is of greater concern in a population that is already iodine deficient or in a borderline status [5,6]. Iodine nutrition status is generally judged by urinary output [5,7,8]. In addition, iodine content of food for infants, notably milk, is of great importance as iodine nutrition affects the neurodevelopment of the young [9–11]. There is thus great interest in trace determination of iodine, particularly in biological fluids such as milk and urine [12,13].

In milk and urine, iodine dominantly exists as iodide. The classical approach to iodine estimation is the kinetically based Sandell–Kolthoff reaction [14] which exploits the catalysis of the oxidation of As(III) with Ce(IV) by iodide. In idealized standards, the reaction can be followed either colorimetrically (Ce(IV) is yellow) or fluorometrically (Ce(III) is fluorescent). However, many other compounds commonly present in biological samples can interfere. Such interferences are typically removed by digesting the sample with chloric acid at 105–115 °C for 30–60 min, however, it is difficult to insure that all interfering species are removed [15]. More recently, digestion with less hazardous ammonium persulfate has replaced chloric acid; it is also easier to use, however, the samples must still be heated to 91–95 °C for 30 min during digestion [16]. Substantial care must be exercised during digestion to prevent the loss of volatile iodine as iodide could potentially be oxidized into iodine by the persulfate. On the positive side, the Sandell–Kolthoff approach is one of the few inexpensively accessible spectrometric approaches that can provide the requisite sensitivity for measuring iodine at low levels in these samples.

Mass spectrometry has long been a formidable tool for qualitative identification; it is also extraordinarily sensitive. Iodine determination by induction coupled mass spectrometry and iodide determination by chromatography–electrospray ionization mass spectrometry have both been widely used. When it comes to quantitative analysis, mass spectrometry is plagued by a number of problems. For accurate quantitation, one must be wary of isobaric interferences and matrix effects [17]. As a general issue in ICP-MS, polyatomic interferences and oxide formation must also

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doi:10.1016/j.talanta.2009.03.038

be avoided. Some of these negative effects can be overcome by specific knowledge of the behavior of the analyte of interest. In ICP-MS, oxide formation can be overcome, for example, by properly choosing operating parameters, such as plasma gas composition, nebulizer flow rate, and radio frequency power [17,18]. Isobaric and polyatomic interferences can be overcome by either monitoring a different isotope of the same element or correcting for the interferant by quantitating it as well [17,19]. In ESI-MS isobaric interferences are typically overcome by preceding the MS with a liquid/ion chromatographic separation technique, which temporally separates the analytes that lead to mass fragments of identical mass to charge ratios (*m*/*z*, hereinafter the unit Thomson (Th) is used, see Ref. [20]). Non-isomeric isobaric interferences that persist in co-eluting after chromatography can be resolved in ESI-MS by tandem mass spectrometry (MS/MS) techniques.

However, the one problem that cannot be solved is effects that arise from variations in the matrix components or as a result of the matrix itself. Matrix effects in MS constitute a more serious problem in two different ways. First, changing levels of electrolytes in the samples cause dramatic fluctuations in the ionization efficiency [21]. This change in ionization efficiency leads to changing signal intensities recorded by the MS. Second, matrix components can deposit in the MS, such as the entrance cones, and cause residue build up. These deposits can block the entrance to the mass analyzer and cause a reduction in signal over time [22,23]. Together or alone, ionization suppression and residue build up can lead to substantial errors. Unless compensated, such errors can amount to an order of magnitude.

Effects from matrix variations and system stability can be corrected by using internal standards (IS) [24]. ISs are purposefully added to all samples and standards at equal concentrations. The IS is a component that is not indigenously present in any sample or is present at negligible concentrations compared to the amount that is added [25]. The IS should also not significantly affect the concentration of the AI present in the sample. The IS is typically added in equal amounts to all standards and samples. For an IS to function correctly, as system or matrix conditions change, any change in the signal attributed to the constant IS concentration must be reflected in a proportionate change in the analyte of interest (AI). The amount of the IS added should not markedly alter the overall sample composition/ionic strength and the IS should be of similar, but not identical, molecular/atomic weight as the analyte of interest [25,26]. The sensitivity of many mass spectrometers varies with the *m*/*z* ratio. Often low *m*/*z* ions are not as easily transferred from the ionization source to the mass analyzer compared to higher *m*/*z* ions [27,28]. In addition, the sensitivity of the instrument for the AI and IS should be similar for the IS to provide correct matrix compensation; this is especially true in ICP-MS. Finally, the IS should behave in a similar way to the AI. In ICP-MS the IS should have a similar first ionization potential to the AI [25,26]. In chromatography–ESI-MS/MS the IS should have an elution time close to that of the AI (ideally co-elute), so it elutes in a similar matrix as the AI. For this same reason, gradient elution should not be used in nonsuppressed ion chromatography (IC) or liquid chromatography (LC) when using an IS that does not fully co-elute with the AI.

Isotope dilution mass spectrometry (IDMS) [29,30] is a special type of internal standardization in MS quantitation. IDMS uses an isotopically modified version of the AI as the IS. Using an isotopically modified version of the AI is the best way to meet all of the requirements of an IS. In perchlorate analysis, using quadruply ^{18}O-labeled perchlorate ($^{35}Cl^{18}O_4$, 107 Th) as an IS has proven, for example, to be the method of choice for quantitation [31,32]. An isotopically labeled IS must, nevertheless, meet the other requirements outlined earlier; in addition, within the experimental duration, the isotopic labeling must be stable [25].

We compare here the performance of several different species used as ISs for iodide/iodine analysis. For IC-MS/MS we compare the performance of $^{35}Cl^{18}O_4$, ^{129}I, and 2-chlorobenzene sulfonate (2-CBS) as internal standards for iodide quantitation. For ICP-MS we compare the performance of ^{72}Ge, ^{115}In, and ^{129}I as ISs for iodine quantitation. In all cases the iodide quantitation data compensated by the appropriate IS are compared to uncorrected values and to each other.

2. Experimental

2.1. Standards and reagents

All solutions were prepared using 18.2 MΩ cm deionized water (Milli-Q Element A10 ultrapure water system, Millipore). Stock standard solutions (1000 mg/L each) of iodine, germanium, and indium were prepared by dissolving 0.1308 g of KI (www.vwrsp.com), 0.1927 g of $InCl_3$ (www.sial.com) and 0.1441 g of GeO_2 (www.Strem.com) in 100 mL of water, 2% HNO_3, and 40 mM NaOH, respectively. A 1.0 mg/L quadruply ^{18}O-labeled perchlorate solution (www.iconisotopes.com) and a 100 nCi carrier-free ^{129}I solution as KI (www.ipl.isotopeproducts.com) were purchased. Based on the certified value of the activity, and the known half-life of ^{129}I (1.57×10^7 years), the 100 nCi K^{129}I solution contained ∼56.6 mg/L ^{129}I. Working solutions of 1.0 mg/L of germanium, indium, and $^{129}I^-$ were prepared by diluting 0.1 mL, 0.1 mL, and 1.765 mL, respectively, to a final volume of 100 mL with water. The 2-CBS solution was prepared in the laboratory from alkaline hydrolysis of the corresponding commercially available sulfonyl chloride (www.sial.com).

2.2. Ion chromatography and ESI-MS/MS

All chromatography was preformed on a Dionex DX-600 ion chromatograph with an IS25 isocratic pump, EG40 eluent generator, an ASRS-Ultra 2-mm suppressor and a CD25 conductivity detector. Chromeleon 6.0 chromatography software was used for system control. Separation was performed on a Dionex IonPac AG-16 (2 mm × 50 mm) guard column and IonPac AS-16 (2 mm × 250 mm) anion separation column. The injection loop volume was 25 μL. The eluent used was 60 mM KOH at a flow rate of 0.25 mL/min. The IC effluent was sent to the ESI-MS/MS.

A ThermoElectron TSQ Quantum Discovery Max MS was used in the negative electrospray ionization mode with a heated electrospray ionization probe (HESI) to increase sensitivity. The MS data was acquired using Xcalibur version 2.0 software package. The HESI probe temperature of the ESI-MS was set at 325 °C, the ion transfer capillary was set at 275 °C and the ionization potential was set at 4.5 kV. The MS operated in the selected reaction monitoring mode (SRM). The monitored ions had SRM *m*/*z* transitions of: 107.0 → 89.0 ($^{35}Cl^{18}O_4^-$), 127.0 → 127.0 ($^{127}I^-$), 129.0 → 129.0 ($^{129}I^-$), and 191.0 → 80.0 (2-CBS, $^{12}C_6H_4{}^{32}S^{16}O_3{}^{35}Cl^-$). Iodide was quantified using the area ratio of iodide to the internal isotopic standard chosen for the correction and compared to a calibration curve composed of AI/IS ratios measured in the prepared standards.

2.3. ICP-MS

An X Series II ICP-MS (www.thermo.com) was used in the direct infusion mode.

The peristaltic pump built into the ICP-MS was used to prime the sample into the Peltier-cooled (3 °C) nebulizer at 1.6 mL/min for 45 s and then continuously aspirate the sample into the nebulizer at 0.8 mL/min. Each measurement cycle consisted of a 20-s qualitative mass survey scan followed by three 32-s long quantitative mass

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