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A comparison of double-focusing sector field ICP-MS, ICP-OES and octopole collision cell ICP-MS for the high-accuracy determination of calcium in human serum

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Abstract

Human serum is routinely measured for total calcium content in clinical studies. A definitive high-accuracy and low-uncertainty method is required for reference measurements to underpin medical diagnoses. This study presents a novel octopole collision cell ICP-MS, high-accuracy, methodology and comparison of that technique with double-focusing sector field ICP-MS and an ICP-OES method. Double-matched isotope dilution mass spectrometry (IDMS) was employed for ICP-MS techniques and an exact matching bracketing technique using scandium as an internal standard was used for ICP-OES analysis. Medium resolution mode was utilised for double-focusing sector field ICP-MS analysis to resolve the dominant interferences on the $^{44}Ca/^{42}Ca$ isotope pair. Hydrogen reaction gas was employed to chemically resolve a number of polyatomic interferences predominantly through charge transfer reactions in the octopole collision cell. Comparison data presented for NIST CRM 909b human serum analysis from all three techniques demonstrates highest accuracy (99.6%) and lowest uncertainty (1.1%) for octopole collision cell ICP-MS. Data from ICP-OES using a non-IDMS technique produces comparably accurate data and low-uncertainties. The much higher total expanded uncertainties for double-focusing sector field ICP-MS compared with octopole collision cell data are explained by lower precision on the measurement of the $^{44}Ca/^{42}Ca$ isotope ratio. Data for octopole collision cell ICP-MS submitted for an international blind trial comparison (CCQM K-14) demonstrated excellent agreement with the mean of all participants with a low expanded uncertainty.
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Keywords: High accuracy; Human serum; Octopole collision cell; IDMS

1. Introduction

Of the total calcium in the body 99% is found in bones and teeth with the remainder in soft tissue and body fluids where it regulates a number of normal body processes [1]. Beneficial Ca functions include: maintenance of healthy teeth and bones, vital component for blood clotting and as a wound-healing agent [1]. Calcium is essential for muscle contraction [2] and helps to control blood pressure and nerve transmission [1]. Calcium deficiency is responsible for an increased risk of hypertension [3,4], arteriosclerosis, alzheimers [5], colon cancer and premenstrual syndrome [4]. Loss of Ca from the bones can result in skeletal deformity [6], osteoporosis and other degenerative joint diseases [5]. Calcium serum levels are additionally measured as an indication of thyroid disease [4] such as primary and tertiary hyperthyroidism and as indicators of Vitamin A and D disorders (both are linked to Ca uptake). It is reported that the normal value for Ca in human serum is $92 \pm 7.3\,\mathrm{ug\,g^{-1}}$ [7] in healthy people (normal renal function and nutritional status).

IMEP 17 (International Measurement Evaluation Programme—Trace and minor constituents in human serum) was an international interlaboratory comparison, which assessed state-of-the-practice Ca measurements from 983 field labs in 35 countries. Selection of Ca as an analyte of

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interest was based on recommendations from the C-AQ IFCC (Committee for the Analytical Quality of the International Federation for Clinical Chemistry and Laboratory Medicine). Results showed a spread of data ranging from 59–106% deviation from the reference value for the sample [8]. It was shown that the combined standard uncertainty of routine measurements is ∼3%.

There is a need to have methods that can accurately determine total Ca in serum with a low-uncertainty, to aid medical diagnosis. These methods can then be used to produce high-quality certified reference materials for the clinical analytical community. Multi-elemental analysis is appropriate when offering a high-quality analytical service; however, for the ultimate accuracy required to produce a high-quality certified reference materials single element, IDMS analysis is important.

In complex matrices such as human serum, Ca analysis is complicated by the existence of interferences and the ubiquitous nature of Ca makes sample preparation and blank contamination major analytical issues. The aims of this study were to produce a high-accuracy isotope dilution mass spectrometry (IDMS) reference value for Ca analysis in human serum by a novel octopole collision cell ICP-MS method and comparison of that technique with double-focusing sector field ICP-MS and non-IDMS ICP-OES analysis. Such comparisons embrace state-of-the art octopole collision cell technology and sector field instrumentation in contrast to the optical detection system employed by ICP-OES. Agreement between three different techniques can only serve to increase confidence in certified reference material values since it is very unlikely that the two different (MS and OES) detection systems will suffer from the same interferences, to the same degree. Such confirmatory supporting data from a second instrument allows us to demonstrate the capability to produce high-accuracy certified reference materials at a suitably low-uncertainty.

2. Method

2.1. IDMS calibrations

High-accuracy analysis by IDMS is now well established [9]. The isotope dilution method utilised for this work here is a modified version of the matching technique originally proposed by Henrion [10] and developed by Catterick and co-workers [11,12]. The technique involves the addition of an isotopically enriched analogue (often referred to as the spike) of the element of interest, which is used as an internal standard. The double-matched IDMS equation as used in this investigation is given in Eq. (1).

$$c'_x = h.c_z \cdot \frac{m_Y}{m_X} \cdot \frac{m_{Zc}}{m_{Yc}} \cdot \frac{(R_Y - R'_B) \cdot R_{Bc}/R'_{Bc}}{R'_B \cdot R_{Bc}/R'_{Bc} - R_X} \cdot \frac{R_{Bc} - R_X}{R_Y - R_{Bc}} \quad (1)$$

where c'_x is the mass fraction of analyte in sample X obtained from one measurement; C_Z is the mass fraction of analyte in primary standard Z; m_Y is the mass of spike Y added to sample X to prepare the blend B (X + Y); m_X is the mass of sample X added to the spike Y to prepare the blend B (X + Y); m_{Zc} is the mass of primary standard solution Z added to the spike Y to make the calibration blend Bc (Bc = Y + Z); m_{Yc} is the mass of spike Y added to the primary standard solution Z to make the calibration blend Bc; R'_B is the measured isotope amount ratio of the sample blend (X + Y); R'_{Bc} is the measured isotope amount ratio of the calibration blend Bc; R_{Bc} is the gravimetric value of the isotope amount ratio of the calibration blend; R_Z is the isotope amount ratio of primary standard Z (IUPAC value [14]) and h is the moisture correction. The use of double IDMS means that we bracket the sample blend B (which contains the sample X, mass m_x, with the spike Y, mass m_y) with a calibration blend Bc (which is prepared by mixing a gravimetric standard Z, mass m_{Zc}, with the spike Y, mass m_{yc}). Each measured isotope R'_B is therefore corrected by the isotope amount ratio R'_{Bc} calculated from the average of the isotope amount ratios of blend Bc measured before and after the sample blend B, a process referred to as bracketing. The matching approach of Catterick [11] was employed with an approximate match made between the spiked calibration blend and the spiked sample blend, which resulted in matching counts per second and isotope ratios to within 5%.

2.2. ICP-OES exact matching bracketing calibration

IDMS analysis cannot be used for ICP-OES analysis because wavelengths are measured rather than masses. Therefore, samples were analysed by ICP-OES using the exact matching bracketing technique described in detail elsewhere [14]. The technique uses a single elemental standard that is prepared to match the analyte concentration (within 5%). A suitable internal standard is then added to both sample and standards to produce a blend. The intensity of Ca internal standard is also matched to give equal signal intensity. The matching of signal intensities between samples and standards, and analyte and internal standard, reduces the uncertainty associated with instrument linearity. The concentration of calcium in the sample was determined according to Eq. (2):

$$C_{smp} = h\left(\frac{I_{smp}/I_{I.S.}}{I_{std}/I_{I.S.}}\right) \times C_{std} \times D \quad (2)$$

where C_{smp} is the amount content of Ca in the serum sample, I_{smp} signal intensity of Ca, $I_{I.S.}$ signal intensity of internal standard, I_{std} signal intensity of the gravimetrically prepared calibration standard, C_{std} concentration of the gravimetrically prepared calibration standard, D the dilution factor prior to analysis and h the moisture correction. The sample was bracketed 10 times with the standard blend for each analytical measurement. The sequence therefore consisted of: blank, mass

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