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Determination of 11 major and minor elements in chondritic meteorites by inductively coupled plasma mass spectrometry

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ABSTRACT

We have developed a new method for the quantification of 11 major and minor elements (Na, Mg, Al, P, S, K, Ca, Cr, Mn, Fe, and Ni) in chondritic meteorites by ICPMS using external calibration with a matrix-matched standard prepared from the Allende Standard Reference Meteorite. We have demonstrated the method's accuracy and assessed three different measures of precision by performing replicate dissolutions and analyses of 0.10-g samples of a homogenized samples of the CM2 meteorite Murchison and compared our results to literature values. We subsequently applied this method to the analysis of a set of four chondritic meteorites possessing a relatively wide range of chondritic compositions with results in accord with previously published values. Because our method is designed to use the same instrumentation and can use samples and standards prepared according to methods previously validated for the determination of a comprehensive suite of minor, trace, moderately and highly volatile trace elements (i.e., Li, Sc, Ti, V, Mn, Co, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, all 14 naturally occurring lanthanoids, Hf, W, Re, Ir, Pt, Tl, Bi, Th, and U) it complements these methods and allows a single laboratory to determine the concentrations of 60 elements in semimicroscopic amounts of chondritic material.

1. Introduction

The abundance of elements in primitive meteorites (i.e., the chondrites) encode unique information about the physical and chemical conditions and processes occurring in the early solar system. Analytical techniques that can accurately and precisely determine comprehensive absolute elemental compositions of bulk meteorite samples are essential for decoding this information. Historically, routine bulk analyses of meteorites have mainly been performed using wet chemical methods [1] or X-ray fluorescence spectrometry (XRF) [2]. These methods typically require large amounts of sample (~20 g for wet chemical analysis, ~5 g for XRF), are destructive, and their sensitivity restricts their application to major and minor abundance elements. Following the Apollo missions of the early 1970s the dominant methodology for bulk meteorite analysis was instrumental neutron activation analysis (INAA) [3]. This method's main strengths include the ability to non-destructively determine the concentrations of a large number of elements, including many major, minor, and trace elements, in semimicroscopic-sized samples (10–100 mg). Because it is non-destructive, it can be combined with radiochemical neutron activation analysis (RNAA) to determine an even larger suite of elements that occur at even lower concentrations [3]. The combination of these two complementary methods has played an important role in cosmochemical studies because the amount of material available for analysis is often limited and meteorites can be heterogeneous on a semimicroscopic level [4]. Interpretation of concentrations of trace elements (e.g., volatile trace elements Bi, Tl, In, and Cd) benefit from knowledge of the major and minor element composition of the specific aliquot analyzed. Interpretations would be affected in the presence of sampling bias. Maximizing the amount of compositional information obtainable from small samples is thus a highly desirable analytical attribute.

Unfortunately, capabilities and facilities to perform such nuclear analytical determinations have generally decreased over the last 20 years ([5], and references therein). Over the last decade, inductively coupled plasma mass spectrometry (ICPMS) has supplanted nuclear methods as the preferred method for the determination of the elemental composition of geological and cosmochemical materials, most commonly for the determination of trace elements [5]. Recently, two methods have been developed that provide the means for the rapid analysis of chondritic meteorites. The method of Friedrich et al. [6] was developed for the determination of a suite of 45 minor, trace, and moderately volatile trace elements (Li, Sc, Ti, V, Mn, Co, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Pd, Sn, Sb, Te, Cs, Ba, all 14 naturally occurring lanthanoids, Hf, W, Re, Ir, Pt, Th, and U). The method of

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Wolf et al. [7] was developed for the determination of a suite of 14 moderately and highly volatile trace elements (Cu, Zn, Ga, Se, Rb, Ag, Cd, In, Sn, Sb, Te, Cs, Tl, and Bi). Five of these elements (Ag, Cd, In, Tl, and Bi) are exclusive to this method. These two methods overcome the difficulty of matrix-induced bias in the ICPMS analysis by utilizing the Allende Standard Reference Meteorite as a matrix-matched standard. Furthermore, because these two methods utilize the same type of instrument (i.e., quadrupole-ICPMS) and can utilize the same prepared samples and standards, together they allow a single laboratory to determine the concentrations of 50 elements in a single semimicroscopic sample of chondritic material.

The goal of this work is to develop and assess an ICPMS-based method, compatible with the methods of Friedrich et al. [6] and Wolf et al. [7], that will allow the reliable determination of 11 cosmochemically important major and minor elements (Na, Mg, Al, P, S, K, Ca, Cr, Mn, Fe, and Ni) in chondritic meteorites so that a more comprehensive analysis can be performed. Here we demonstrate our method and assess its precision and accuracy. This method utilizes internal standardization via addition of Be and In and multiple single point matrix-matched external calibrations to provide drift corrected calibration within the ICPMS procedure. We demonstrate our method's precision and accuracy by performing replicate dissolutions and analyses of 0.1-g samples of a homogenized sample of the CM2 meteorite Murchison and compare our results to literature values for this meteorite. We subsequently apply this method to the analysis of four different types of chondritic meteorites that span a relatively wide range of chondritic compositions: Orgueil (CI), Tagish Lake (C2), Bruderheim (L6), and Krymka (LL3). In all cases our results are in accord with previously published values. Because this method utilizes the same instrumentation and can use samples and standards prepared as described by Friedrich et al. [6] and Wolf et al. [7], it allows a single laboratory to determine the concentrations of 60 major, minor, trace, moderately, and highly volatile trace elements in semimicroscopic amounts of chondritic material.

2. Experimental

2.1. Meteorite standard and sample preparation

Four carbonaceous chondrite meteorites, Allende (CV3), Murchison (CM2), Tagish Lake (C2), and Orgueil (CI), and two ordinary chondrite meteorites, Bruderheim (L6) and Krymka (LL3) were used in this study. Aliquots of Allende Standard Reference Meteorite powder (US National Museum, USNM 3529, split 22, position 22) were used as received to prepare matrix-matched calibration standard solutions. Method validation solutions were prepared from aliquots of powder sampled from a 50-g homogenized whole-rock specimen of Murchison (US National Museum, USNM 5453). We prepared a 0.30-g whole-rock powdered sample of Bruderheim (Field Museum, B93) and a 0.60-g whole-rock powdered sample of Orgueil (#247) from chips using an agate mortar and pestel. Krymka (Smithsonian Meteorite Powders Collection), which had previously been homogenized, separated into metallic and non-metallic fractions, and analyzed by Jarosewich [1] was recombined and sampled. An aqueous aliquot of Tagish Lake that had been dissolved via microwave digestion at Purdue University [6] was analyzed directly subsequent to dilution and addition of internal standard. All sample handling and preparation was performed in a dedicated trace element hood under class 100 conditions.

Dissolution of powdered solids followed the closed-vessel procedure outlined in Wolf et al. [7]. All chemical reagents and materials utilized were identical to those described in Wolf et al. [7] including >18-MΩ cm water and Optima grade acids (Fisher Scientific International). All stock and prepared reagents were stored in pre-cleaned, triply rinsed Teflon FEP bottles. Prior to analysis, dissolution blanks, dissolved meteorite standards and samples were stored in similarly treated 50-mL polypropylene conical centrifuge tubes. All sample and solution preparation was performed gravimetrically. Triplicate 0.1-g powder aliquots of Murchison were dissolved for our study. Duplicate 0.1-g powder aliquots of Allende were dissolved to ensure the availability of sample calibration standard solution. Single 0.1-g aliquots of Tagish Lake, Orgueil, Bruderheim, and Krymka were dissolved for our study. After dissolution and dilution to 50-g of total solution as described in Wolf et al. [7], 0.25-g of a 20 μg mL^{-1} Be and 2 μg mL^{-1} In mixed internal standard spike prepared from 1000 μg mL^{-1} single element standards (Spex Certiprep, Metuchen, NJ, USA) was added to 5-, 10-, and 25-g aliquots of blank, standard, and sample solutions. These solutions were subsequently diluted to 50 g with 5% (v/v) HNO_3. The final solutions contained nominally 100 ng mL^{-1} Be and 10 ng mL^{-1} In. These final standard and sample solutions contained 0.02%, 0.04%, or 0.1% total dissolved solids (TDS). Dissolution blanks, standards, and samples were then analyzed on a quadrupole ICPMS (PQ Excell, Thermo Electron Corporation, Waltham, MA, USA) at the Indiana State University Trace Element Laboratory using an ICPMS instrumentation described in Wolf et al. [7]. Daily instrument set-up routine followed that described in Wolf et al. [7] and operating conditions are given in Table 1.

Table 1
ICPMS operating conditions and measurement parameters.

Parameter	Operating range
RF power	
Forward	1350 W
Reflected	<5 W
Gas flows	
Cooling	14.0 L min^{-1}
Auxiliary	0.90 L min^{-1}
Nebulizer	0.80–0.84 L min^{-1}
Ion lens settings	
Extraction	-700 to -350 V
L1	-4.5 to $+2.9$ V
L2	-81.0 to -71.0
L3	-105.0 to -93.9 V
D1	-39.0 to -34.2 V
Focus	$+26.7$ to $+33.6$ V
Pole bias	$+1$ to $+3$ V
Vacuum system	
Expansion pressure	1.0–1.5 mbar
Analyzer pressure	6×10^{-7}–9×10^{-7} mbar
Sensitivity at $m/z=115$[a]	6–8 $\times 10^4$ cps
Stability (10×60-s acquisitions)[a]	$<2\%$ RSD
Background at $m/z=220$[a]	<0.03 cps
Ce^{2+}/Ce^{+}[a]	<0.04
CeO^{+}/Ce^{+}[a]	<0.02
Data acquisition	
Mass analysis mode	Peak jumping
Channels per mass	1
Dwell time	10 ms
Acquisition time	60 s

[a] Determined for 1 ng mL^{-1} Be, Mg, Co, Ni, In, Ce, Bi, Pb, and U tuning solution.

2.2. ICPMS methodology

Each ICPMS analysis procedure was performed following the general protocol of bracketing groups of samples between calibration blocks. Each calibration block consisted of a calibration

Table 2
Allende calibration values and uncertainties (1s) for the 11 major and minor elements determined in this work as reported by Jarosewich et al. [9]. Analytical masses, LOQs for solid samples, and range of concentrations previously measured in chondritic meteorites for the 11 major and minor elements determined in this work.

Element	Masses monitored	Allende ($mg\ g^{-1}$) [b]	LOQ, solid ($mg\ g^{-1}$)[c]	Chondrites ($mg\ g^{-1}$)[d]
Na	23	3.42 ± 0.09	0.03	3.3–7.0
Mg	25[a], 26	148.3 ± 1.2	0.004	97–153
Al	27	17.3 ± 0.4	0.02	8.1–17.5
P	31	1.07 ± 0.05	0.01	0.85–2.00
S	33, 34[a]	21.0 ± 0.03	4	20–58
K	39	0.31 ± 0.05	0.2	0.310–0.825
Ca	44	18.4 ± 0.5	0.004	8.5–19.0
Cr	52, 53[a]	3.6 ± 0.1	0.0002	2.65–3.88
Mn	54	1.50 ± 0.09	0.00008	1.45–2.62
Fe	57	235.7 ± 0.8	0.005	182–275
Ni	60[a], 62	14.2 ± 0.2	0.0008	10.2–17.5

[a] Analytical mass used for quantitation.

[b] Recommended values reported by Jarosewich et al. [9] with elemental concentrations calculated from oxides for Na, Mg, Al, P, S, K, Ca, Ca, Cr, and Mn.

[c] LOQ ($10s_{blank}$) calculated using the pooled standard deviation of triplicate analyses of procedural blank solutions measured prior to first sample and after the last sample three separate procedures. Concentration equivalent assuming 0.1-g of meteorite dissolved and diluted to a 0.1% TDS solution.

[d] Range of mean values (low–high) for CI, CM, CO, CV, H, L, LL, EH, and EL chondrites reported in Wasson and Kallemeyn [10].

blank and standard. Dissolution blanks were used as the calibration blanks and dissolved Allende Standard Reference Meteorite solutions were used as the matrix-matched calibration standards. Standards and samples contained equivalent %TDS. At most, three samples were analyzed between calibration blocks. This pattern was repeated not more than three times per analysis procedure. Calculation of elemental concentrations was performed using the method of internal standardization with external calibration utilizing a first order sensitivity versus time correction calculated for each sample from the two calibration blocks bracketing the samples [8]. Calibration values and their associated uncertainties are listed in Table 2 [9].

Prior to assessment of the overall analytical method, scoping experiments were performed to establish two critical experimental parameters for our method: the optimal sample dilution factor and the specific isotope or isotopes to use for quantitation of multi-isotopic elements (e.g., Mg, S, Ca, Cr, Fe, and Ni). These scoping experiments followed our general analysis protocol and used Allende Standard Reference Meteorite solutions as both calibration standard and sample. Three scoping procedures were performed, one each with standards and samples diluted 0.02%, 0.04%, and 0.1%TDS. These procedures were used to calculate method limits of quantitation (LOQ) and establish instrument limits of linearity (LOL) for element isotopes given in Table 2.

Subsequent to establishing these experimental parameters, we assessed accuracy and precision of our method with both samples and standards at the determined optimal TDS value. To achieve this we performed nine replicate analyses on each of the three replicate dissolved Murchison samples in a series of three analytical procedures. These three procedures were performed on three different days following daily routine instrument warm-up and set-up procedures described in Wolf et al. [7]. Each of the three samples was then analyzed in triplicate in each procedure with each replicate bracketed by separate calibration blocks. This experimental design facilitated assessment of within-sample precision, between-sample precision, and between-procedure precision for all 11 elements.

3. Results and discussion

3.1. Analysis parameter selection

Selecting optimal dilution factors and isotope(s) used for the basis of elemental quantitation in our method is based on the criteria that overall method accuracy is achieved under analysis conditions in which signal-to-noise (S/N) ratio is maximized for each element. Signal levels must also be maintained below the ICPMS LOL. Selecting parameters that are optimal for all 11 elements and allow simultaneous analysis is considered an asset, but not a requirement. The suite of elements considered in this work span four orders of magnitude in concentration in chondritic meteorites (Table 2). Several elements (S, Ca, K, and Fe) possess relatively large ICPMS backgrounds due to polyatomic interference and need to be determined at relatively high isotopic concentration to sufficiently exceed these backgrounds. Obtaining sufficient signal is not a significant issue for Na, Mg, Al, P, Ca, Cr, Mn, Fe, and Ni. In fact, the signal of the most abundant elements Mg and Fe need to be minimized with respect to other elements in our suite to a level below ICPMS LOL ($\sim 10\ \mu g\ mL^{-1}$ for a monoisotopic element, depending on element ionization efficiency and instrument conditions). Dilution to lower TDS levels is an obvious approach and has the additional advantage of decreasing instrument matrix effects and thus improving instrument stability and method accuracy. However, dilution compromises the accuracy of K and S determination. Potassium abundances are relatively low in chondritic materials (Table 2) and dilution decreases the concentration of this important volatile lithophile element: decreasing the accuracy of its determination. Sulfur determination is also problematic. Despite its relatively high abundance in chondritic materials, high background originating from polyatomic ion interference on its highest abundance isotope (e.g., ^{16}O, $^{16}O^+$ on $^{32}S^+$) and low ionization efficiency (10.4 eV) necessitates selection of an alternative minor isotope such as ^{33}S or ^{34}S for quantitation thus, effectively lowering its measureable signal. Performing multiple analyses at different TDS levels is an option. Fortunately both Mg and Fe possess isobar-free minor isotopes (e.g., ^{25}Mg and ^{57}Fe, respectively) and their isotopic concentrations can be effectively decreased by using these isotopes as the basis for elemental quantitation without excessive dilution. This effectively increases the concentration range of a single analysis. Using ^{57}Fe as the basis for Fe quantitation has the additional advantage of enhancing S/N due to a lower polyatomic ion background than $^{56}Fe^+$ experiences with ^{16}O, $^{40}Ar^+$.

Table 1 gives limits of quantitation (LOQ), defined as $10s_{blank}$ expressed in units of $mg\ g^{-1}$ element for a 0.1-g sample dissolved and diluted to 0.1%TDS for the 11 elements considered. Results of our three scoping experiments demonstrate that at 0.1%TDS Mg and Al concentrations are close to ICPMS LOL and would exceed this limit in some chondritic meteorites. At 0.02%TDS all elements are above LOQ for typical chondritic meteorites however S and K concentrations are within an order of magnitude from this limit and their quantitation would be expected to be less accurate. Dilution of dissolved Allende Standard Reference Meteorite and chondritic samples to 0.04%TDS along with selection of the isotopes indicated in Table 1, best meet our analytical requirements. This dilution factor and set of isotopes are used in our validation experiments on chondritic samples.

3.2. Method precision

We used the CM2 chondrite Murchison to assess the precision and accuracy of our method. Murchison fits several requirements for this purpose: ample material is available, it has been demonstrated

Table 3
ICPMS within-procedure precision, between-procedure precision, and between-sample precision for the 11 major and minor elements determined in this work.

Element	Within-procedure precision (%-RSD)	Between-procedure precision (%-RSD)	Between-sample precision (%-RSD)
Na	0.41	0.46	0.96
Mg	0.42	0.78	4.8
Al	0.56	0.76	1.2
P	1.4	1.6	1.4
S	2.8	3.1	1.8
K	2.4	2.6	1.8
Ca	0.55	0.66	1.1
Cr	0.08	0.41	2.9
Mn	0.20	0.40	1.2
Fe	0.12	0.41	1.2
Ni	0.46	0.65	0.87

Table 4
ICPMS results for the 11 major and minor elements and their accuracy expressed as %-relative difference compared to a compiled literature mean values [13–22] and from a single lab [13]. Numbers in parenthesis are the number of literature references used to calculate mean and 1s standard deviation.

Element	Murchison this work (mg g^{-1})	Murchison literature (mg g^{-1}) [a]	Accuracy %-relative error	Murchison literature (mg g^{-1}) [b]	%-relative error
Na	3.78	2.9 ± 1.3 (8)	+32	3.51	+7.8
Mg	119	120 ± 5 (6)	−1.1	126	−5.9
Al	11.8	11.8 ± 0.7 (6)	+0.25	12.8	−7.9
P	0.979	1 (2)	−2.1	N.D.	N.D.
S	34.5[c]	30.5 ± 3.8 (3)	+13	N.D.	N.D.
K	0.342	0.31 ± 0.06 (7)	+12	0.405	−16
Ca	12.7	13.1 ± 1.1 (7)	−2.9	14.5	−12
Cr	3.17	3.11 ± 0.23 (7)	+2.1	3.09	+2.6
Mn	1.73	1.66 ± 0.08 (7)	+4.4	1.76	−1.6
Fe	212	212 ± 6 (7)	+0.17	209	+1.6
Ni	12.9	13.3 ± 0.8 (5)	−3.6	12.0	+7.2

[a] Average and standard deviation compiled from the following sources [13–22] except for the following omissions: P [16], S [17].

[b] Kallemeyn and Wasson [13].

[c] When analyzed at 0.1% TDS, a value of 31.8 mg g^{-1} is obtained with a +4.4% relative difference from the mean literature value.

to be very homogeneous even at the trace element level [11], and a reasonable amount of composition data exist. Table 3 lists three measures of precision calculated for the 11 elements determined in this work when standards and samples were prepared to 0.04%TDS: within-procedure precision, between-procedure precision, and between-sample precision. Precision values for individual elements are expressed as percent relative standard deviation (%-RSD) and are calculated so that the experimental factors analytical procedure and sample replicate are considered independently [12].

The ICPMS within-procedure precisions, a measure of repeatability of analysis of the same sample in a single procedure, range from 0.08%- to 2.8%-RSD with a mean of 0.86%-RSD when all 11 elements are considered as a suite. Within-procedure precisions for all elements were <0.6%-RSD with the exception of the two elements possessing the lowest S/N ratios, S and K. These elements had within-procedure precisions of 2.8%- and 2.4%-RSD, respectively. The ICPMS between-procedure precisions, a measure of repeatability of analysis of the same sample on different days, range from 0.40%- to 3.1%-RSD with a mean of 1.1%-RSD when all 11 elements are considered as a suite. One-way analysis of variance (ANOVA) for the factor procedure reveals that only S shows a significant variability (probability <0.05) between procedures. From the standpoint of practical application however, this variability is tolerable. The ICPMS between-sample precision, a measure of sample homogeneity and/or repeatability of preparation, range from 0.87%- to 4.8%-RSD with a mean of 1.7%-RSD when all 11 elements are considered as a suite. One-way ANOVA for the factor sample reveals that all elements except S and K show a significant variability between our three samples. Because the differences in mean elemental concentrations of the 11 elements of our three samples do not reveal a monotonic trend, this variability between samples is most likely due to minor compositional heterogeneity between our powdered aliquots. That a significant difference is not observed for S and K is most likely due to the fact that a lower S/N ratio for the determination of these elements obscures any real compositional variation. Our results however, demonstrate that our ICPMS methodology is sufficiently precise to discriminate between samples with relatively small compositional differences. In general, the overall mean precision demonstrated by this method is comparable to INAA [13].

3.3. *Method accuracy*

A comparison of mean results of our analyses of Murchison when standards and samples are prepared to 0.04% TDS with mean literature values is given in Table 4. The means and standard deviations for previously published values for each element are calculated based on a comprehensive search of available literature [13–22]. This compilation is composed of data that are primarily derived from wet chemical analysis and INAA. When a single literature value differed from the group mean by >1 s, the datum was excluded from our compilation.

Comparison of our ICPMS results to mean literature values shows that all 11 elements determined in this work are within ±1 s of their respective literature means. Eight elements (Mg, Al, P, Ca, Cr, Mn, Fe, and Ni) are within ±5% relative to the literature mean. Na, S, and K are +32%, +13%, and +12% relative to their mean literature values, respectively. When all 11 elements are considered as a suite the mean relative deviation from the mean literature values is 6.6%.

Because of the important role that it plays in cosmochemical processes, establishing that our method could be used for the determination of S is particularly desirable. Sulfur analysis is usually performed using a dedicated technique such as combustion infrared spectrometric analysis (C-IR) or wet chemical gravimetric analysis, if sufficient material is available. Alternatively, sector-based high resolution (HR)-ICPMS has been applied to the analysis of S isotopes. Moderate resolution ($m/\Delta m = 4000$) is capable of resolving polyatomic ion interferences and increasing S/N ratio for S analysis. The use of quadrupole-based ICPMS equipped with collision reaction cells has also demonstrated the capability of minimizing spectral interferences via elimination of oxide interferences [23]. In the case of S, Table 4 shows that our result is +13% relative to the literature mean. However, when a second aliquot of our dissolved sample and the standard Allende was prepared to 0.1% TDS and reanalyzed, we obtained 31.8 mg g^{-1}. This corresponds to +4.4% relative to the literature mean. We attribute this result to an improvement in S/N for ^{34}S at this lower dilution factor. When this value is used for S the mean relative deviation from the mean literature values for all 11 elements is reduced to 5.8%. Accordingly, optimal S analysis could be performed at this lower dilution factor at the expense of requiring an additional procedure provided sufficient solution is available.

Several potential reasons exist for Na and K to have relatively greater deviations from mean literature values than our other lithophile analytes. While Na provides a sufficient signal when the Allende Standard Reference Meteorite standard and Murchison are prepared to 0.04% TDS, it typically possesses a relatively high instrumental background due to its tendency to adsorb to the ICPMS liquid sample introduction components. Sodium therefore requires a significant blank subtraction which can potentially add uncertainty to the resulting analysis. In the case of K, low concentrations in chondritic materials result in lower S/N ratios relative to other analytes. However, when we prepared our standards and samples to 0.1% TDS and performed a reanalysis, we obtained results indistinguishable from those prepared at 0.04% TDS for both Na and K. Our Na and K results most likely represent real bias with respect to our compiled literature values. Other explanations for these differences are feasible. Literature values for Na and K in Murchison are highly variable: 44%- and 19%-RSD, respectively. Potassium also possesses a relatively large uncertainty in concentration in the Allende Standard Reference Meteorite (16%-RSD). Because these concentrations are the basis of our calibrations for these elements, uncertainties in these values propagate through our results. Comparison of our results to those from analyses of 250–350 mg aliquots of Murchison from a single laboratory [13] using a single method (INAA) show a more favorable comparison for Na. In this case Na is +7.8% to relative to the literature value. Six other elements (Mg, Al, Cr, Mn, Fe, and Ni) are also within ±10% of the reported mean values. Ca and K are −12% and −16% relative to the literature mean, respectively. P and S were not determined by INAA. When all 9 elements available for comparison are considered as a suite the mean relative deviation from Kallemeyn and Wasson [13] is 6.9%. Given that the mean uncertainty of the concentrations used for calibration is 12%-RSD and the surprisingly wide range of literature values for Murchison, our method provides results that are in accord with literature values and is comparable to INAA [13].

3.4. Method application to chondritic meteorites

Table 5 shows comparisons of major and minor element concentrations in the carbonaceous chondrites Orgueil, Tagish Lake and the ordinary chondrites Bruderheim and Krymka as determined by our method to previously published values. Literature values for Bruderheim and Krymka represent literature compilations in which data has been selected using the same >1 s criteria that was used for Murchison. Results that differ by more than 10% from literature values are listed in italics.

For all elements the accuracy of our results for carbonaceous chondrites Orgueil and Tagish Lake are comparable to our Murchison analyses. For Orgueil all 11 elements determined are within ±10% of values published by Anders and Grevesse [24]. Eight elements (Na, Mg, Al, Ca, Cr, Mn, Fe, and Ni) are within ±5% of the literature value. When all 11 elements are considered as a suite the mean relative deviation from literature values is 3.7%.

For Tagish Lake all 11 elements determined are within ±10% of values published by Brown et al. [25]. Eight elements (Na, Mg, Al, P, Ca, Mn, Fe, and Ni) are within ±5%. When all 11 elements are considered as a suite the mean relative deviation from the literature values is 3.4%. The accuracy of the results for both of these carbonaceous chondrites reflect the fidelity to which the standard matches the composition of the samples and also undoubtedly, the relative homogeneity of carbonaceous chondrites.

For the L6 ordinary chondrite Bruderheim our results are more variable. Nine of the 11 elements determined are within ±10% of the mean of compiled literature values; seven of these elements (Na, Mg, Al, S, K, Ca, and Fe) are within ±5% [1,20,26–32]. Phosphorus and Ni exceed ±10% (−30% and +13%, respectively). Our P literature mean is based on wet chemical analyses from three labs performed more than 50 years ago [26,27,29]. A single more recent wet chemical analysis of a homogenized 20-g specimen by Jarosewich [1] gave a value of 0.916 mg g^{-1}. While our value is in accord with this more recent wet chemical analysis, this value was excluded from our database due to our outlier criteria. Our Ni result (+13%) is potentially consistent with sampling bias given that our sample was prepared from a homogenized 0.30-g chip and Ni's siderophile tendency to concentrate in dispersed reduced iron phases. A slightly higher Fe value in our aliquot supports this hypothesis, but a more complete analysis would be required to determine the extent of this sample's heterogeneity. Comprehensive replicate analyses of 20 chips of Bruderheim by Haas and Haskin [28] using INAA yield a value of 14.72 mg g^{-1}. Again, while our value of (14.5 mg g^{-1}) is in accord with this more modern INAA result, the Haas and Haskin [28] value was excluded from our database due to our outlier criteria. These levels of bias for P and Ni are not evident in results for our other samples. Notable also is our Cr result which is −7.9% relative to the literature mean. This negative bias could

Table 5

Results of analyses of 11 major and minor elements in carbonaceous chondrites Orgueil, Tagish Lake and the ordinary chondrites Bruderheim and Krymka. Numbers in parenthesis are the number of literature references used to calculate mean and 1s standard deviation. Numbers in italics are results that exceed ±10% relative to the literature mean.

Element	Orgueil this work (mg g^{-1})	Orgueil literature (mg g^{-1})[a]	Tagish Lake this work (mg g^{-1})	Tagish Lake literature (mg g^{-1})[b]	Bruderheim this work (mg g^{-1})	Bruderheim literature (mg g^{-1})[c]	Krymka this work (mg g^{-1})	Krymka literature (mg g^{-1})[d]
Na	4.75	4.90	4.32	4.45 ± 0.06	7.12	7.2 ± 0.3 (6)	6.25	6.1 ± 0.1 (2)
Mg	99.1	95.3	107	108 ± 5	146	149.7 ± 0.8 (4)	145	150 ± 1 (2)
Al	8.86	8.69	10.3	9.9 ± 0.3	11.7	11.6 ± 0.8 (3)	11.6	11.6 ± 0.1 (2)
P	1.26	1.18	0.929	0.927 ± 0.050	*0.87*	1.24 ± 0.03 (3)	0.96	0.92 ± 0.06 (2)
S	56.3	52.5	34.1	38 ± 2	22.2	23.3 ± 0.7 (3)	22.9	22.0 ± 0.2 (2)
K	0.532	0.566	0.611	0.650 ± 0.050	0.92	0.94 ± 0.10 (5)	*0.88*	0.77 ± 0.03 (2)
Ca	8.87	9.02	10.1	9.9 ± 0.9	12.5	12.9 ± 0.2 (4)	12.6	13.4 (2)
Cr	2.76	2.66	2.69	2.84 ± 0.15	3.35	3.6 ± 0.2 (5)	3.64	3.76 ± 0.09 (2)
Mn	2.02	1.98	1.46	1.45 ± 0.15	2.67	2.5 ± 0.1 (4)	2.62	2.59 ± 0.04 (3)
Fe	181	185.1	188	193 ± 9	230	228 ± 6 (6)	187	188.2 ± 0.3
Ni	10.8	11.0	11.3	11.6 ± 0.5	*14.5*	13 ± 1 (6)	10.0	9.75 ± 0.07 (2)

[a] Anders and Grevesse [24].

[b] Brown et al. [25].

[c] Average and standard deviation compiled from [1,20,26–32] except for the following omissions: Na [31], Mg [20], Al [26], P [1], S [29], K [29], Ca [26], Cr [26], Mn [31], Fe [31], and Ni [28].

[d] Average and standard deviation compiled from [33–35] except for the following omissions: Na [35], Mg [35], Al [33], K [33], Ca [35], Cr [33], Fe [33], and Ni [33].

potentially be the result of incomplete dissolution of refractory Cr containing phases such as chromites or other spinels by our mineral acid-based methodology. When all 11 elements are considered as a suite the mean relative deviation from the literature values is 6.6%.

Accuracy of results for the unequilibrated LL3 ordinary chondrite Krymka are comparable to those of our carbonaceous chondrites: 10 of 11 elements determined were within ±10% our literature compilation [33–35]. Nine elements (Na, Mg, Al, P, S, Cr, Mn, Fe, and Ni) are within ±5%. Only K was not within ±10% with a relative error of +14%. Similar to Bruderheim, Krymka shows a slight negative Cr bias with respect to the literature mean. When all 11 elements are considered as a suite the mean relative deviation from the literature values is 3.9%.

4. Conclusions

We have developed a new method for the quantification of 11 major and minor elements (Na, Mg, Al, P, S, K, Ca, Cr, Mn, Fe, and Ni) in chondritic meteorites by ICPMS. The method utilizes internal standardization via addition of Be and In and external calibration with the Allende Standard Reference Meteorite. Multiple calibrations bracket samples to provide drift corrected calibration within the ICPMS instrumental analytical procedure. Accurate determination of these elements has been achieved by diluting dissolved samples to specific TDS levels and where appropriate, selecting minor isotopes to effectively extend the concentration range of a single analysis or to maximize the S/N ratio of a particular element. While all 11 elements can be determined in a single analysis, determination of elements possessing particularly lower S/N ratios (i.e., S and K) can be made at higher TDS levels. We have demonstrated our method's accuracy and assessed three different measures of precision by performing replicate dissolutions and analyses of 0.10-g samples of a homogenized sample of the CM2 meteorite Murchison and compared our results to literature values with good agreement. We subsequently applied this method for the analysis of four different types of chondritic meteorites that span a relatively wide range of chondritic compositions: Orgueil (CI), Tagish Lake (C2), Bruderheim (L6), and Krymka (LL3). In all cases our results were in accord with previously published values. Because this method utilizes the same instrumentation and can use samples and standards prepared as described by Friedrich et al. [6] and Wolf et al. [7], it allows a single laboratory to determine the concentrations of 60 major, minor, trace, moderately and highly volatile trace elements in semimicroscopic amounts of chondritic material.

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References

[1] E. Jarosewich, Meteoritics 25 (1990) 323–337.
[2] H. Von Michaelis, L.H. Ahrens, J.P. Willis, Earth Planet. Sci. Lett. 5 (1969) 387–394.
[3] E. Anders, R. Wolf, J.W. Morgan, M. Ebihara, A.B. Woodrow, M.J. Janssens, J. Hertogen, US DOE Office of Science and Technical Information, NAS-NS-3117, Washington, DC, 1988.
[4] M.E. Lipschutz, D.S. Woolum, J.F. Kerridge, M.S. Mathews (Eds.), Meteorites and the Early Solar System, University of Arizona Press, Tucson, Arizona, 1988, pp. 462–487.
[5] M.E. Lipschutz, S.F. Wolf, F.B. Culp, A.J.R. Kent, Anal. Chem. 79 (2007) 4249–4274.
[6] J.M. Friedrich, M.-S. Wang, M.E. Lipschutz, Geochim. Cosmochim. Acta 67 (2003) 2467.
[7] S.F. Wolf, D.L. Unger, J.M. Friedrich, Anal. Chim. Acta 528 (2005) 121–128.
[8] ThermoElemental, VG PlasmaLab Reference Guide, Version 1.06, Cheshire, UK, 2000.
[9] E. Jarosewich, R.S. Clarke Jr., J.N. Barrows, Smithsonian Contrib. Earth Sci. 27 (1987) 1–49.
[10] J.T. Wason, G.W. Kallemeyn, Philos. Trans. R. Soc. A 325 (1988) 535–544.
[11] M.E. Zolensky, R.H. Hewins, D.W. Mittlefehldt, M.M. Lindstrom, X. Xiao, M.E. Lipschutz, Meteoritics 27 (1992) 596–604.
[12] American Society for Testing and Materials, ASTM Standard D 691-11, 14.02, 2011, West Conshohocken, Pennsylvania, 2011.
[13] G.W. Kallemeyn, J.T. Wasson, Geochim. Cosmochim. Acta 45 (1981) 1217–1230.
[14] R. Burgess, I.P. Wright, C.T. Pillinger, Meteoritics 26 (1991) 55–64.
[15] G. Dreibus, H. Palme, B. Spettel, H. Wänke, Meteoritics 28 (1993) 343.
[16] W.D. Ehmann, D.E. Gillum, J.W. Morgan, R.A. Nadkarni, T.V. Rabagay, P.M. Santoliquido, D.L. Showalter, Meteoritics 5 (1970) 131–136.
[17] L.H. Fuchs, E. Olsen, K.J. Jensen, Smithsonian Contrib. Earth Sci. 10 (1973) 1–39.
[18] M.M. Grady, A.L. Graham, D.J. Barber, D. Aylmer, G. Kurat, U. Ott, T. Ntaflos, H. Palme, B. Spettel, Mem. Natl. Inst. Polar Res. (Tokyo), Spec Issue 46 (1987) 162–178.
[19] E. Jarosewich, Meteoritics 6 (1971) 49–52.
[20] N. Nakamura, Geochim. Cosmochim. Acta 38 (1974) 757–775.
[21] D.L. Showalter, H. Wakita, R.A. Schmitt, Meteoritics 7 (1972) 295–301.
[22] F. Wlotzka, B. Spettel, H. Palme, L. Schultz, Meteoritics 24 (1989) 341–342.
[23] D.R. Bandura, V.I. Banerov, S.D. Tanner, Anal. Chem. 74 (2002) 1497–1502.
[24] E. Anders, N. Grevesse, Geochim. Cosmochim. Acta 53 (1989) 197–214.
[25] P.G. Brown, A.R. Hildebrand, M.E. Zolensky, M. Grady, R.N. Clayton, T.K. Mayeda, E. Tagliaferri, R. Spalding, N.D. MacRae, E.L. Hoffman, D.W. Mittlefehldt, J.F. Wacker, J.A. Bird, M.D. Campbell, R. Carpenter, H. Gingerich, M. Glalatiotis, E. Greiner, M.J. Mazur, P.J. McCausland, H. Plotkin, T.R. Mazur, Science 290 (2000) 320–325.
[26] H. Baadsgaard, F.A. Campbell, R. Folinsbee, G.L. Cumming, J. Geophys. Res. 66 (1961) 3374–3577.
[27] M.B. Duke, D. Maynes, H. Brown, J. Geophys. Res. 66 (1961) 3557–3563.
[28] J.R. Haas, L.A. Haskin, Meteoritics 26 (1991) 13–26.
[29] H. König, Geochim. Cosmochim. Acta 28 (1964) 1697–1703.
[30] O. Müller, P.A. Baedecker, J.T. Wasson, Geochim. Cosmochim. Acta 35 (1971) 1121–1137.
[31] R.A. Schmitt, G.G. Goles, R.H. Smith, T.W. Osborn, Meteoritics 7 (1972) 131–214.
[32] F. Tera, O. Eugster, D.S. Burnett, G.J. Wasserburg, Proceedings of the Apollo 11 Lunar Science Conference, Geochim. Cosmochim. Acta 34 (Suppl. 1) (1970) 1637–1657.
[33] M.I. Dyakonova, V.Y. Kharitonova, Meteoritika 18 (1960) 48–67.
[34] E. Jarosewich, R.T. Dodd, Meteoritics 16 (1981) 83–91.
[35] G.W. Kallemeyn, A.E. Rubin, D. Wang, J.T. Wasson, Geochim. Cosmochim. Acta 53 (1989) 2747–2767.