High accuracy method for isotope dilution mass spectrometry with application to the measurement of carbon dioxide

Martin J.T. Milton*, Jian Wang

National Physical Laboratory, Analytical Science Group, Teddington TW11 0LW, UK

Abstract

A new approach to the quantitative analysis by isotope dilution mass spectrometry (IDMS) has been developed that overcomes many of the limitations of established methods. It incorporates additional dilution steps that act as an internal calibration so that an independent isotopic reference material is not required. It avoids the need to measure the isotope ratio of the highly enriched spike directly, and enables the final results to be arranged as a combination of measurements that are largely insensitive to instrumental bias and drift. Consequently, it has the potential to extend the scope of application of IDMS to include analyses for which reference materials with certified isotope ratios are not available or where contamination of the instrument by the highly-enriched spike causes difficulty. The new method has been demonstrated by measuring the mass ratio of an isotopically-enriched sample of carbon dioxide in a natural sample of carbon dioxide with a relative uncertainty of 0.02%. (Int J Mass Spectrom 218 (2002) 63–73). Crown Copyright © 2002 Published by Elsevier Science B.V. All rights reserved.

Keywords: Isotope dilution mass spectrometry (IDMS); Two-step IDMS; Isotope ratio mass spectrometry; Carbon dioxide

1. Introduction

The accurate measurement of the concentration of standard gas mixtures presents a challenge to analytical science. This arises because standards can be prepared with values traceable to their gravimetric composition with relative uncertainties of the order 10^{-4}, but there are no widely available matrix-independent methods capable of analysis with comparable uncertainty. Isotope dilution mass spectrometry (IDMS) has the potential to play such a role in the analysis of trace metals and organics [1–3] but has not been proven in

applications to gas analysis demanding the smallest uncertainties.

In its basic form, IDMS requires measurements of the isotope ratios of a sample, a highly enriched spike and a blend (or "isotope mixture") of the two [4]. The wide range of isotope ratios that these span is challenging to measure with an accuracy of better than 1% without the use of an external calibration. It has therefore become common practice to rely on reference materials with certified isotope ratios to calibrate the response of the spectrometer at particular mass numbers [5–7]. However, this is only feasible when suitable traceable reference materials are available with valid estimates for their uncertainty. Advances in the IDMS method include the development of the two-step IDMS method [8,9] which extends the direct (or "one-step")

---

* Corresponding author.
E-mail: martin.milton@npl.co.uk, jian.wang@npl.co.uk

method by the introduction of a "reverse" step, in which the enriched spike is blended with a pure material with the same isotope ratio as the sample. This eliminates the need to measure the concentration of the pure spike and reduces the range of mass numbers at which the isotope ratio must be measured to just two. However, there is still a need to measure the isotope ratio of the highly enriched spike, which is undesirable because of the risk of contamination and the difficulty of carrying out accurate measurements over an extended range of isotope ratios. The "exact matching" method [8,9] relies on the use of a reverse blend that is closely matched to the unknown blend, this minimises the dependence of the results on the isotope ratio of the enriched spike, but does not eliminate it entirely and may require an iterative process to approach the optimum condition.

In this paper, we introduce a new formulation of the IDMS method that uses a single mathematical curve to relate the isotope ratio of all possible blends of any stated pair of sample and spike materials. Our formulation extends beyond the work of others who have reported an isotope dilution curve [6] based on a linear assumption, which significantly limits the accuracy of the results. The insight from the full isotope dilution curve developed here gives much more flexibility in the design of IDMS methods than is provided simply by numerical solutions [10].

We propose a new method that extends the "two-step" method by the introduction of a second reverse step which leads to a result that is entirely independent of any measurement of the isotope ratio of the spike. In this case, all of the isotope ratio measurements can be chosen to be within a limited dynamic range which can be close to the abundance of the natural sample. The uncertainty of the method has been verified by making a series of blends of natural and highly-enriched carbon dioxide and comparing the results of the new IDMS method with the mass ratios of the gases in the blends derived from their gravimetric preparation. The application of this new method will be to the measurement of standard gas mixtures with an accuracy of better than 0.1%. These are required for a number of applications including

verifying trends in the concentration of carbon dioxide in the ambient atmosphere for the investigation of globe warming. Many such applications will require cryogenic trapping of a matrix gas (such as nitrogen) out of the sample in order to carry out isotope dilution on the required analyte [11]. We have chosen to demonstrate the capability of the new method at the highest possible level of accuracy by using pure gases [12] in order to avoid the uncertainty introduced by any cryogenic trapping procedure.

2. Isotope dilution mass spectrometry methods

The basic principle of IDMS is that an amount N_1 of sample is blended with an amount N_{sp1} of an enriched spike, the isotope ratio of the resulting blend (R_{b1}) is then related to the isotope ratios of the spike (R_{sp}) and sample (R_s) by [4,5,9]:

$$\frac{N_1}{N_{sp1}} = \frac{R_{sp} - R_{b1}}{R_{b1} - R_s} \frac{\sum_i R_s}{\sum_i R_{sp}} \tag{1}$$

where the summations are over all isotopes of the species being measured. Introducing the quantities x, Q and δ (defined in Table 1), Eq. (1) can be rewritten:

$$x_1 = \frac{\delta_{sp} - \delta_{b1}}{\delta_{b1}} Q \tag{2}$$

Eq. (2) is the basic measurement equation that applies to each isotope dilution step within any IDMS procedure. Every possible isotope dilution between the same spike and sample with isotope ratios R_{sp} and R_s that define $\delta_{sp} = (R_{sp}/R_s - 1) \times 1000$ corresponds to a point on a curve defined by (2) with x and δ_b being the dependant and independent variables. The form of this curve becomes more familiar by re-arranging (2) into the form:

$$(x + Q)\delta_b = Q\delta_{sp} \tag{3}$$

This is the equation of the rectangular hyperbola shown in Fig. 1. The values of x and δ_b for any possible blend created from the same sample and spike correspond to a single point on this curve. The curve crosses the δ_b axis at δ_{sp} since $x = 0$ corresponds to

Table 1
Symbols

Symbol (unit)	
N_i (mol)	Amount of sample in the ith blend, $i = 1, 2$ and 3
N_{spi} (mol)	Amount of spike in the ith blend, $i = 1, 2$ and 3
R_s, R_{sp}	Isotope amount ratio in sample and spike
R_{bi}	Isotope amount ratio in the ith blend, $i = 1, 2$ and 3
δ_{sp}	$(R_{sp}/R_s - 1) \times 1000$
δ_{bi}	$(R_{bi}/R_s - 1) \times 1000$, $i = 1\ 2$, and 3
M_s, M_{sp} (g/mol)	Molar mass of sample and spike
Q	$M_s/M_{sp} \cdot \Sigma R_s / \Sigma R_{sp}$, the summations are over all isotopes
m_i, m_{spi} (mg)	Masses of sample and spike for the ith blend, $i = 1, 2$ and 3
x_i	m_i/m_{spi}, $i = 1, 2$, and 3
x_{IDMS}	Value of amount ratio m_1/m_{sp1} obtained by IDMS
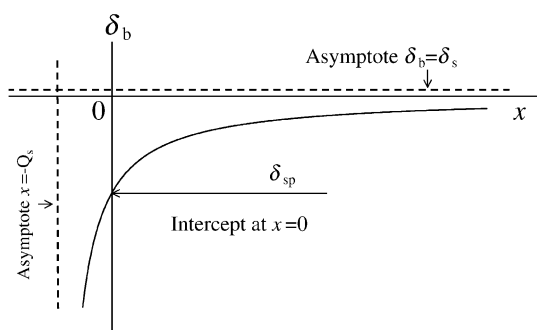
Fig. 1. General isotope dilution curve (for the case of $R_{sp} < R_s$).

a "blend" that only contains the pure spike. The curve tends to an asymptotic value of $\delta_b = 0$ as $x \to \infty$ which corresponds to a hypothetical "blend" with no spike.

When the two parameters δ_{sp} and Q are known, the curve in Fig. 1 is defined completely through Eq. (3). For example, Fig. 2 shows the curve for stated values of δ_{sp} and Q. Alternatively, since the curve is defined by an equation with two unknown parameters, it can be defined completely from knowledge of the co-ordinates of any two points that lie on it. These known points could be the results, for example, of two
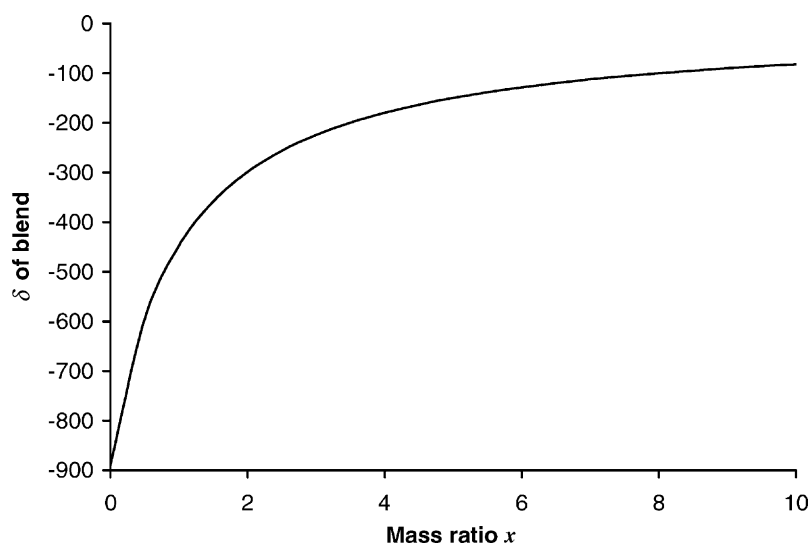
Fig. 2. Isotope dilution curve for the spike and sample used for the validation experiments ($\delta_{sp} = -890.429$ and $Q_s = 1.01098$).
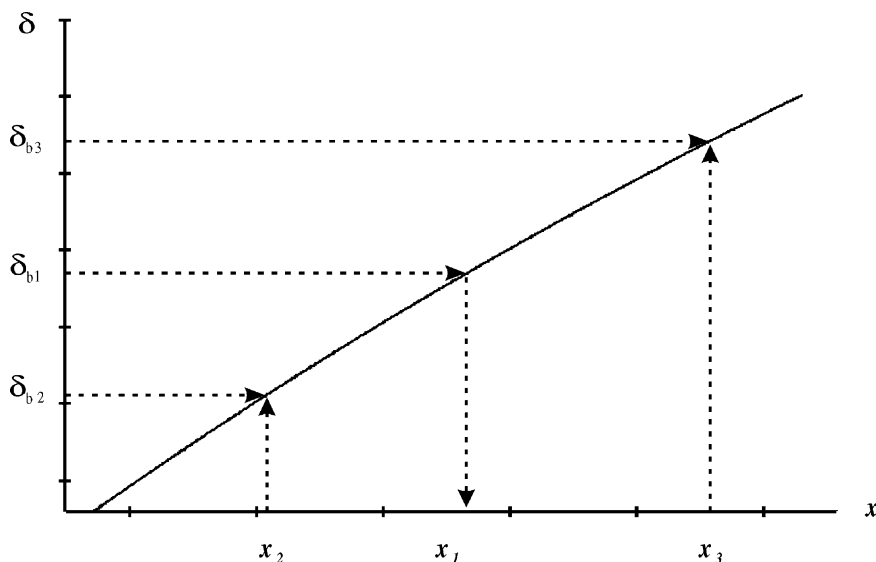
Fig. 3. Enlarged section of the isotope dilution curve (Fig. 2).

"reverse" steps in which the spike is blended with a pure material with the same isotopic composition as the unknown. Once the curve is defined, a measurement of the value of δ_b for an unknown blend will correspond to a single point on the curve with a corresponding value for x (Fig. 3). It is important to notice that our approach combines the quantities R_s and R_{sp} into the variable δ_{sp} and similarly R_s and R_{bi} into δ_{bi}. Hence, it is necessary to measure three quantities (R_s and R_{sp} and Q) in order to define the two parameters (δ_{sp} and Q) that determine the isotope dilution curve.

In the case of the "two-step" IDMS method, a "reverse" step is introduced that involves a second blend consisting of an amount N_2 of pure material of the same isotopic composition (the "back spike") as the sample and an amount of enriched spike N_{sp2}. Applying (2) to the reverse step leads to:

$$x_2 = \frac{\delta_{sp} - \delta_{b2}}{\delta_{b2}} Q \tag{4}$$

If the natural isotopic composition of the unknown varies, an additional factor must be introduced to allow for any difference between it and the back spike [13]. In this work, we consider the case where the influence of this factor is negligible. Eqs. (2) and (4) can

be combined to eliminate Q and produce the measurement equation for the two-step IDMS method:

$$x_1 = x_2 \left(\frac{\delta_{b2}}{\delta_{b1}} \right) \left(\frac{\delta_{sp} - \delta_{b1}}{\delta_{sp} - \delta_{b2}} \right) \tag{5}$$

In this paper we propose a new method that incorporates a further reverse step, in which a third blend is made from an amount of pure material N_3 and an amount of enriched material N_{sp3}. Applying (2) again leads to:

$$x_3 = \left(\frac{\delta_{sp} - \delta_{b3}}{\delta_{b3}} \right) Q \tag{6}$$

Eqs. (2), (4) and (6) can now be manipulated to eliminate the unknown terms δ_{sp} and Q and rearranged to give:

$$x_1 = Dx_2 + (1 - D)x_3 \tag{7}$$

where

$$D = \frac{\delta_{b2}(\delta_{b3} - \delta_{b1})}{\delta_{b1}(\delta_{b3} - \delta_{b2})}$$

As mentioned above, this formula applies when the isotopic composition of the unknown sample is the same as that of the reference. When this is not the case,

a further parameter must be introduced into Eq. (7) [13]. The new method presented here is not based on the same principle as the "double-spike method" developed previously for multi-isotopic species such as iron [14,15]. Our method uses two different blends and depends on analysis at only two mass numbers.

The IDMS method described by Eq. (7) has some important characteristics. Firstly, it has the benefit that it does not involve the parameter Q used in Eq. (2) which is extremely difficult to measure directly. Secondly, it does not require any direct measurement of the un-diluted spike, which avoids any risk of contaminating the instrument. Thirdly, it only involves measurements of the quantity δ which can be chosen to fall within a limited range of isotope ratios in order to minimise the effect of instrumental non-linearity. Finally, all of the δ measurements are configured in pairs such that the final result is dependant on a ratio of δ values (δ_{b2}/δ_{b1}), and a ratio between the differences of δ values $[(\delta_{b3} - \delta_{b1})/(\delta_{b3} - \delta_{b2})]$. This configuration not only enables the cancellation of inherent "scale contraction" due to memory effects [16,17], but also makes the final results less sensitive to any systematic error in the measured values due to equilibriation or mass fractionation processes [18]. These lead to one of the most important properties of the new method which is that it enables the isotope ratios to be chosen such that the instrument does not require external calibration. Hence it can be used to measure unknown samples for which no isotopic reference materials are available. The only requirements are the availability of an enriched spike material of the same species and a pure back spike with the same isotopic composition as the unknown. The spike material is only required for the manufacture of the blends—it is not necessary to have any information about its isotope ratio.

3. Experimental section

3.1. Gravimetry and preparation of the blends

A number of blends were prepared for the purpose of validating the new method using ^{13}C-depleted CO_2
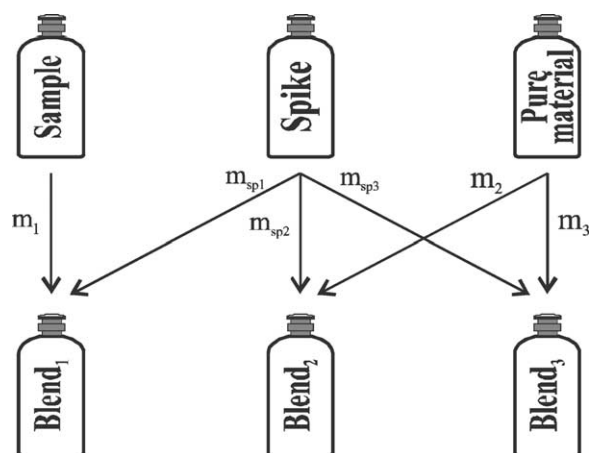

Fig. 4. Scheme for preparation of blends.

(^{12}C, 99.95%, Cambridge Isotope Laboratories, MA, USA) and natural CO_2 (SFC grade N5.5, BOC Special Gases, Guildford, UK). ^{13}C-depleted material was used in preference to ^{13}C-enriched material in order to limit the exposure of the equipment to high level of ^{13}C. The scheme for preparation of blends is as shown in Fig. 4. A validated procedure for making primary gas standards gravimetrically was used to form the blends [19]. Two identical 500 ml stainless steel cylinders (Swagelok®) with identical valves were used for storing and weighing the gas mixtures. One was filled with air at atmospheric pressure and designated as the tare and the other was used for the sample. The sample cylinder was evacuated before the first weighing cycle and then filled successively with spike and sample in the second and third weighing cycles. During each weighing cycle, the difference in mass between the sample cylinder and the tare cylinder was recorded five times using a single-pan mass comparator (Mettler-Toledo PR2004) following a conventional A-B-B-A substitution method. The resolution of the balance was 0.1 mg and the repeatability of the weighings was 0.2 mg or better. The masses of the sample m and spike m_{sp} were calculated from the results of the successive weighing cycles. The expanded uncertainty for each value of m and m_{sp} was calculated to be 1 mg ($k = 2$) corresponding to a combination of the uncertainty of the two successive weighings with that

from the buoyancy correction [20,21]. In the experiments reported here the masses of the samples were in the range 48.5–50.5 g and the masses of spike added were in the range 9.0–10.0 g.

3.2. Instrumental and measurement procedure

The isotope ratio measurements were carried out on a modified Optima mass spectrometer (Micromass, Wythenshawe, UK). The principle modification is the use of two dual-inlet sample introduction systems. Each inlet had an automated $100\,cm^3$ stainless steel bellows to control and balance the pressures between the inlets. This configuration is ideal for carrying out the measurements of δ for the three blends required for the new IDMS method. The periods of time for which the instrument was exposed to each of the gas samples and subsequently evacuated were carefully optimised in order to reduce the influence of memory effects and hence to increase the precision. Important set up parameters are shown in Table 2. A multiple collector assembly capable of simultaneous measurements at masses 44, 45, 46 and 47 was used for the measurements reported here. The extent of isobaric interference at these masses is extremely small compared with the magnitude of the ion current from the analyte ions. All of the results presented here refer to the ratio of 45/44 since the signals corresponding to 46, 47 are significantly smaller for the samples used here. An unusual feature of the isotope ratio measurements reported here is that the ratio of 45/44 has been used rather than the more common $^{13}C/^{12}C$ ratio. This is because there is no need to reduce the measured data to equivalent values for the isotopes of the constituent elements in order to use IDMS in the absence of isotopic equilibriation process.

Table 2
Selected data acquisition parameters for the four channel mass spectrometer

Integration time	60 s
Sum of ion currents at 44 and 45	11 nA
Accelerating voltage	3.8 kV
Analyser vacuum	$<5 \times 10^{-7}$ mbar
Mass resolution	100

In this experiment, one of the four inlets was used for the natural abundance sample which served as the reference for measuring the blends in terms of the quantity δ. The other three inlets were used for the blends which were measured sequentially. The control software allowed a conventional alternating measuring sequence of "... reference/sample/reference ..." to be performed between pairs of gas samples in any order. The values for each δ reported here are calculated from an average of 10 repeat measurements of the isotope ratio of the blend and the natural sample. The standard deviation of these 10 measurements is typically 1×10^{-4} relative to value. The IDMS results reported here are based on an average of nine repeated measurements of each δ made from a single filling of the bellows.

4. Results and discussion

The analysis of the principle of IDMS presented in Section 2 shows that if a set of three blends is made from the same sample and spike, then their mass ratios (x_i) determined from gravimetry together with their corresponding δ_{bi} values will satisfy Eq. (7) and correspond to three points on the curve shown in Fig. 1. However, in any real measurement, experimental errors in both the gravimetry and the isotope ratio measurement will lead to discrepancies between the two sides of the equation. Since gravimetry is a primary method which yields results that are traceable to the SI [22], we use it to provide "reference" values against which the new method can be validated.

The results presented in the following sections make use of a set of blends prepared gravimetrically with mass ratios of the enriched to natural CO_2 in the range 4.8–5.6 (as summarised in Table 3).

4.1. Consistency of isotope ratio measurement

It is generally expected that the values of δ measured on a mass spectrometer are subject to error primarily because of instrument drift and mass fractionation effects in the gas inlet. Fig. 5 illustrates the

Table 3
Gravimetric values of four blends used in the validation of the new method

	Quantity			
	x_2	x_3	x_1	x_1'
Value	5.51972	4.81652	4.97971	5.28783
U	0.00062	0.00050	0.00052	0.00058
Relative uncertainty	0.011%	0.010%	0.010%	0.011%

U represents the expanded uncertainty with a coverage factor k of 2.

variations around the mean values of δ measured for each of three blends. These were recorded by changing our previously described measurement procedure to incorporate a standby time of 4 h between the measurements of each set of three δ, so that any drift in the results would be larger than experienced during our IDMS measurements. Fig. 5 shows that the fractional change in the measured value of δ can be as large as 5×10^{-4} over 64 h, which is approximately five times larger than the uncertainty of each value. This change is a consequence of mass fractionation processes in each of the inlets [18]. These largely

occur at the crimp where molecular flow results in a conductance that is proportional to $M^{-1/2}$. Consequently, the lighter species escapes through the crimp into the source quicker than the heavier species with a consequent increase in the ratio of 45/44. When the bellows is refilled from the sample cylinders, the measured value of δ returns to the unfractionated level.

4.2. Uncertainty of the method

The uncertainty of the method can be estimated by the application of the internationally-accepted method [20] to the measurement Eq. (7). This results in an expression for the uncertainty of the result $u(x_1)$ in terms of the uncertainty of the amount ratios of the two reverse blends [$u(x_2)$ and $u(x_3)$] and the uncertainty of the measurements of the three δ values [$u(\delta_1)$ etc.]. The results of this analysis are shown in Table 4. It can be seen that the estimate of the combined uncertainty of the result is 0.00083, and that the contributions of each of the five terms are of the same order of magnitude.
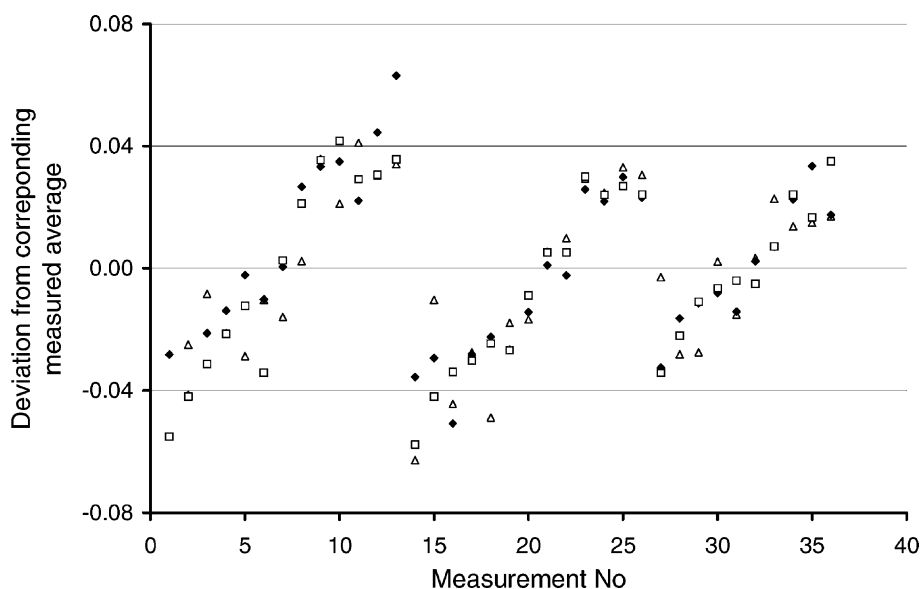

Fig. 5. Repeated measurements of δ for the three blends allowing a 4 h delay between each. Each δ value reported is an average of 10 measurements of each isotope ratio and has a typical standard deviation of 2×10^{-5}. Each point on the graph corresponds to the deviation from measured average for each loading. The bellows supplying gas to each inlet were re-filled after measurements 11 and 26.

Table 4
Gravimetric values and IDMS results for the first set of blends

	Value	Expanded uncertainty	Contribution to combined uncertainty
x_2	5.51972	0.00062	0.00014
x_3	4.81652	0.00050	0.00038
δ_1	−157.394	0.015	0.00057
δ_2	−144.458	0.015	0.00016
δ_3	−161.799	0.015	0.00042
x_{IDMS}	4.98047		0.00083

Fig. 6 shows the IDMS results calculated from the data shown in Fig. 5 using Eq. (7). The value derived during the gravimetric preparation of the "unknown" blend is shown as a reference. It demonstrates that during the 64-h period during which the isotope ratio measurements drifted by 0.008%, the standard deviation relative to the value of the IDMS method was only 0.012%. Additionally, the systematic nature of the drift seen in Fig. 5 is not reflected in Fig. 6. This confirms that the results of the new IDMS method are largely insensitive to the systematic drift observed in the mass spectrometer.

4.3. Validation of the new IDMS method

Three blends were chosen from the set prepared gravimetrically to validate the capability of the new method to measure an "unknown". One of the blends was designated as the "unknown" and the mass ratio determined during its preparation was used as the reference to be compared with the IDMS result. In order to validate the uncertainty of the new method and check its consistency, this measurement was repeated five times. The results are shown in Fig. 7. The mean of the five IDMS results is slightly larger than the gravimetric "reference" value, but falls well within the estimated uncertainty. The relative uncertainty of each measurement is approximately 0.02% and the relative difference between the mean of the five IDMS results and the gravimetric result is 0.007%. Similar results were generated when these measurements were repeated using the second set of blends. The uncertainty of the new method is nearly one order of magnitude smaller than reported previously for the analysis of CO_2 in air by one-step IDMS [11] and the analysis of synthetic mixtures of Xe [12].
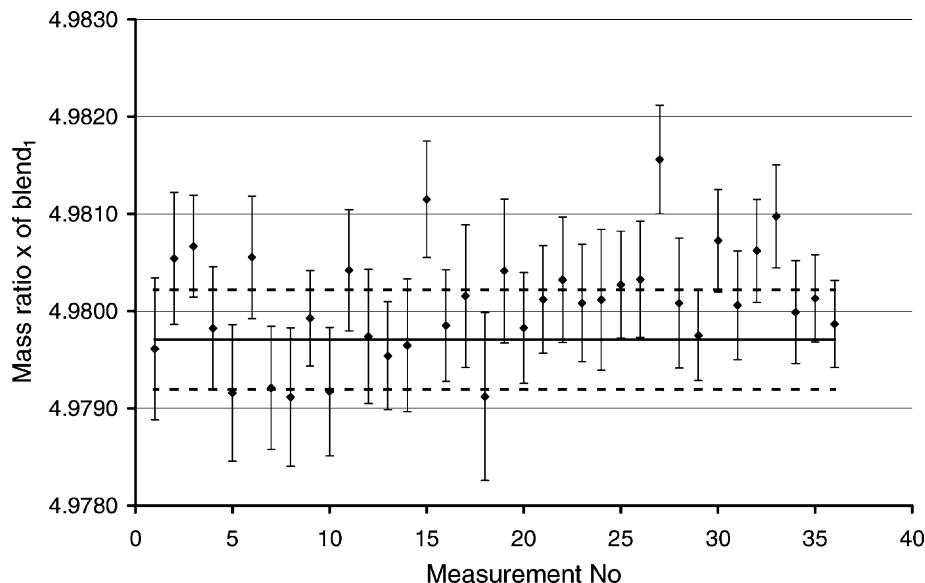

Fig. 6. Results of IDMS analysis from blends measured in Fig. 5. One of the blends has been considered as "unknown" and its gravimetric value is shown as a reference. The solid line indicates the gravimetry value for the "unknown" and the dotted lines indicate the uncertainty ($k = 2$).
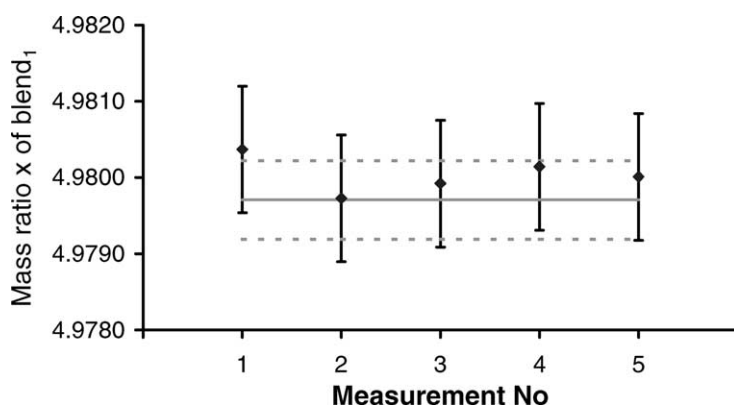
Fig. 7. Results of five repeat analyse using the IDMS method described here. The solid line indicates the gravimetry value for the "unknown" and the dotted lines indicate the uncertainty ($k = 2$).

4.4. Validation of isotope dilution curve

The results of the new IDMS method can also be displayed by plotting the gravimetric mass ratio and corresponding δ value for each of the blends on an isotope dilution curve. Fig. 8 shows the isotope dilution curve passing through two measured points. Additionally, we show the data for a third and fourth blend (made from the same sample and spike) on the same curve. Fig. 9 shows a detailed view of one of these points with its corresponding uncertainties. It can be seen that it is consistent with the isotope dilution curve within its estimated uncertainties. This confirms the validity of the isotope dilution curve approach. An interesting feature of measurements made from the isotope dilution curve is that their uncertainty can be
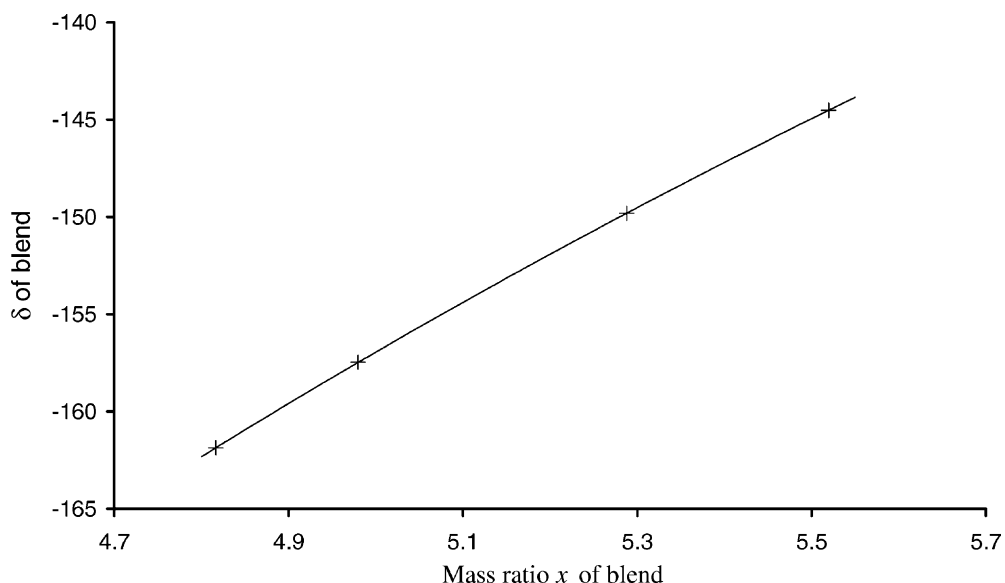

Fig. 8. Isotope dilution curve for the experimental results reported here. The curve passes through x_2 and x_3. The observations of the "unknowns" x_1 and x_1' are also shown.
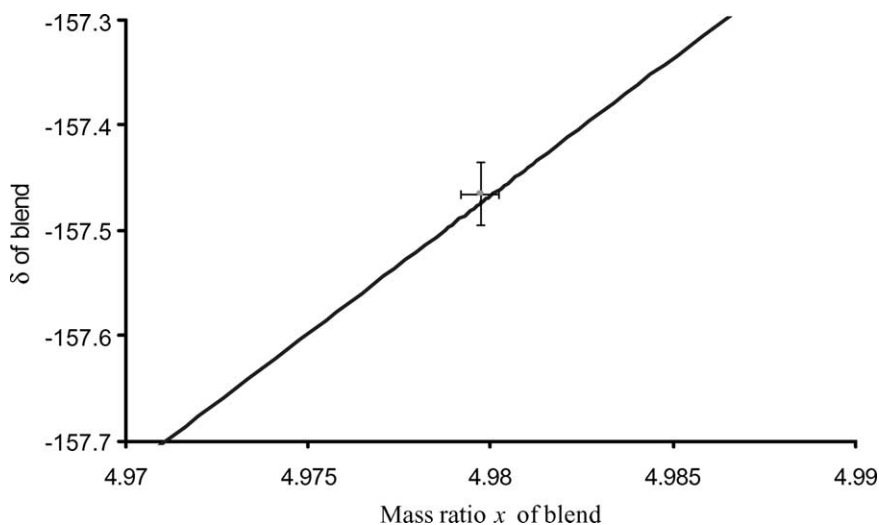
Fig. 9. Detailed isotope dilution curve near to the "unknown" point x_1 in Fig. 8.

reduced below the uncertainty of a single gravimetric value $u(x)$ by $\sqrt{N}$ (where N is the number of points used to define the line).

4.5. Applications of the isotope dilution curve

As discussed in Section 2, the isotope dilution curve also provides means for measuring the isotope ratio of the spike. For example, δ_{sp} can be calculated using the measured values of (x_2, δ_{b2}) and (x_3, δ_{b3}) in Table 4 as:

$$\delta_{sp} = -\frac{(x_3 - x_2)\delta_{b2}\delta_{b3}}{x_3\delta_{b3} - x_2\delta_{b2}} = -910.1$$

If the isotopic composition of the pure CO_2 used in the experiment is known, then the isotope ratio of R_{sp} is given by:

$$R_{sp} = \left(\frac{\delta_{sp}}{1000} + 1\right) R_s$$

The value of Q, which must be measured in one step IDMS, can also be determined from the isotope dilution curve. Using the same set of data (x_2, δ_{b2}) and (x_3, δ_{b3}) in Table 4:

$$Q = -\frac{x_3\delta_{b3} - x_2\delta_{b2}}{\delta_{b3} - \delta_{b2}} = 1.0411$$

This approach is significantly simpler than measuring the summations over all isotopes of the species being measured directly and can provide a basis for comparisons with the absolute isotope ratio measurements required for one-step IDMS [12].

5. Conclusion

We have developed and validated a new IDMS method that uses two "reverse" or "internal calibration" steps. The measurement equation is new and, in addition to the gravimetric mass ratio measurement, only consists of measurements of the quantity δ which expresses the isotope ratio of each blend relative to that of the unknown sample. All the measurements of δ can be chosen to be within a limited dynamic range and no isotope ratio measurements of the spike are required. Hence the final results are insensitive to inherent scale contraction effects, due to memory or other non-linear effects, and drift in measurement of δ. The result is not dependent on any absolute isotope ratios and therefore does not require certified isotopic reference materials to calibrate the response of the mass spectrometer.

We have validated the new method by a series of measurements of blends of isotopically-enriched

carbon dioxide in natural carbon dioxide. The relative uncertainty in the analysis of one blend is estimated to be 0.02%. This confirms that the new method offers new possibilities for the use of IDMS in high-accuracy analysis of gases. The principle of this new method is also applicable to elemental and organic IDMS measurements and has the potential to be a primary method which will give results that are traceable to SI units [22].

Acknowledgements

References

[1] P. Klingbeil, J. Vogl, W. Pritzkow, G. Riebe, J. Müller, Anal. Chem. 73 (2001) 1881.
[2] P. Klemens, K.G. Heumann, Fres. J. Anal. Chem. 371 (2001) 758.
[3] N. Demuth, K.G. Heumann, Anal. Chem. 73 (2001) 4020.
[4] M. Riepe, H. Kaiser, Fres. J. Anal. Chem. 233 (1966) 321.
[5] K.G. Heumann, in: F. Adams, R. Gijbels, R.V. Grienken (Eds.), Inorganic Mass Spectrometry, Wiley, New York, 1988.
[6] J.F. Pickup, K. McPherson, Anal. Chem. 48 (1976) 1885.
[7] P. Evans, C. Wolff-Briche, B. Fairman, J. Anal. At. Spectrom. 16 (2001) 964.
[8] A. Henrion, Fres. J. Anal. Chem. 350 (1994) 657.
[9] M.J.T. Milton, R.I. Wielgosz, Metrologia 37 (2000) 199.
[10] L. Siekmann, H. Breuer, J. Clin. Chem. Clin. Biochem. 20 (1982) 883.
[11] R.M. Verkouteren, W.D. Dorko, Anal. Chem. 61 (1989) 2461.
[12] Y. Aregbe, S. Valkiers, K. Mayer, P. De Bievre, R.M. Wessel, A. Alink, Metrologia 35 (1998) 7.
[13] M.J.T. Milton, J. Wang, P. Harris, NPL Report COAM 7, March 2002.
[14] M.H. Dodson, J. Sci. Instrum. 40 (1963) 289.
[15] C.M. Johnson, B.L. Beard, Int. J. Mass Spectrom. 193 (1999) 87.
[16] H.A.J. Meijer, R.E.M. Neubert, G.H. Visser, Int. J. Mass Spectrom. 198 (2000) 45.
[17] W.G. Mook, P.M. Grootes, Int. J. Mass Spectrom. Ion Processes 12 (1973) 273.
[18] I.T. Platzner, Modern Isotope Ratio Mass Spectrometry, Wiley, Chichester, 1977.
[19] ISO 6142 Gas analysis—Preparation of calibration gas mixtures—Gravimetric method, 2001.
[20] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP and OIML. Guide to the Expression of Uncertainty in Measurement. ISBN 92-67-10188-9, 2nd Edition, 1995.
[21] M.J.T. Milton, P. Holland, C. Brookes, P. Woods, A.J. Davenport, NPL Report COEM 60, April 2001.
[22] M.J.T. Milton, T.J. Quinn, Metrologia 38 (2001) 289.