

A comparison of high accuracy isotope dilution techniques for the measurement of low level sulfur in gas oils

Ruth Hearn^{a,*}, Michael Berglund^b, Markus Ostermann^c, Nusa Pusticek^b, Philip Taylor^b

^a LGC, Queens Road, Teddington, Middlesex TW110LY, UK

^b Institute for Reference Materials and Measurements, Commission of the European Communities, JRC, Retieseweg, B-2440 Geel, Belgium

^c Bundesanstalt für Materialforschung und prüfung (BAM), Unter den Eichen 87, D-12205 Berlin, Germany

Received 16 September 2004; received in revised form 18 October 2004; accepted 18 October 2004

Available online 28 December 2004

Abstract

A comparison of high accuracy methods for the analysis of total sulfur in gas oils by three metrology institutes is described. The work contains a comparison of three different aspects of the analysis: sample digestion, instrumental measurement and isotope dilution strategies.

Thermal ionisation mass spectrometry (TIMS) in combination with high pressure ashers (HPA) or Carius tube digestion has traditionally been used for such high accuracy analysis. However, this paper demonstrates that the faster, less laborious technique of ICP-MS in combination with microwave digestion is equally capable. Results from the comparison experiments show excellent agreement for fuel samples containing sulfur concentrations in the range 11–200 $\mu\text{g g}^{-1}$. This excellent agreement across the different sample preparation, measurement and isotope dilution techniques has been exploited in the certification of two new diesel fuel reference materials.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Sulfur; Gas oil; Isotope dilution; ICP-MS; TIMS; Uncertainty

1. Introduction

Environmental concerns about sulfur emissions from the burning of fossil fuels led to legislation related to the sulfur content. In 1993, the EC legislation for sulfur content was 500 and 2000 $\mu\text{g g}^{-1}$ for petrol and diesel fuels, respectively [1]. The current limits (set in 1998) are 150 and 350 $\mu\text{g g}^{-1}$, respectively, and the limit for both fuels is set to be reduced to just 50 $\mu\text{g g}^{-1}$ by the year 2005 [2]. In addition to the environmental concerns, it is now recognised that sulfur content in fuel can reduce the efficiency of catalysts containing the platinum group elements such as those in car exhaust catalysts. These two concerns have increased the demand for fuel containing sulfur at less than 10 $\mu\text{g g}^{-1}$. It is anticipated that the 10 $\mu\text{g g}^{-1}$ maximum sulfur concentration for road transport fuels will become mandatory in the EU from 2009. It is necessary to ensure that sufficient quantities of petrol and

diesel fuels with a maximum sulphur content of 10 $\mu\text{g g}^{-1}$ are available from 1 January 2005 on an appropriately balanced geographical basis. Moreover, the planned and already achieved goals on lowering the sulfur content in fuels necessitate improved measurement techniques.

The industry has a number of recognised methods for the determination of sulfur in fuel [3]. The most common technique used by fuel companies to check sulfur in gas oil is combustion followed by UV fluorescence. Other techniques include X-ray fluorescence or high temperature combustion followed by IR detection or iodometric titration of SO_2 . As the demand for lower level analysis increases, these industry methods require the support of high accuracy methods that can provide reference values and certified reference materials with low uncertainties at these diminished concentrations. These can then be used to validate and maintain industry methods at low levels.

One such high accuracy method for the sulfur concentration in gas oils has been isotope dilution (ID) followed by thermal ionisation mass spectrometry (TIMS) [4,5].

* Corresponding author. Tel.: +44 20 8943 7644; fax: +44 20 8943 2767.
E-mail address: ruth.hearn@lgc.co.uk (R. Hearn).

The inductively coupled plasma mass spectrometer (ICP-MS) is increasingly being implemented as a tool for fast and precise isotope ratio measurements. Results for ICP-MS measurements of sulfur have been published by Prohaska et al. [6], Hearn and Evans [7], Yu et al. [8], Mason et al. [9] and Menegário et al. [10].

Both TIMS and ICP-MS require acid digestion of fuel samples prior to the measurement of sulfur. Three different sample digestion procedures have been presented in the literature: Carius tube combustion [5], high pressure asher digestion (HPA) [4] and microwave digestion (MW) [7,11]. The Carius tube and the HPA digestion methods in combination with TIMS are considered as robust techniques as they are well established for this type of analysis [4,5]. This study will focus on the comparison of these techniques with the more recent techniques of MW digestion and ICP-MS. In this study results from three metrology institutes (BAM, LGC, and IRMM) will be presented.

2. IDMS methodologies

The methodologies for isotope dilution used in this study have been described in detail elsewhere [4,12]. In brief, isotope dilution involves the addition of an isotopically enriched analogue (often referred to as the spike) to the sample. This isotopic analogue is able to act as the ideal internal standard since it has the same chemical properties as the analyte to be determined. The isotopic abundances in both the sample and the spike must be well characterised and the sample and spike must be fully equilibrated in solution. The measurement of the ratio of isotopes in the prepared sample will then allow accurate quantification of the concentration of analyte in the sample.

The method used by LGC [12] is referred to as “exact matching double IDMS”, which requires the use of a well-defined calibration standard of natural, preferably certified, isotope abundances. However, the concentration in the isotopically enriched spike does not need to be exactly defined.

The method used by IRMM and BAM [4] is referred to as “single IDMS”. This method requires a spike material that is well characterised for concentration and isotope abundances.

3. Experimental

3.1. Samples and reagents

A comparison of the methods has been made using LGC candidate reference materials (supplied by BP Chemicals, Sunbury, UK), a BCR certified reference material and a dilution of NIST SRM3154 sulfuric acid standard solution (labelled MOS). In addition, the microwave digestion method and ICP-MS method have been validated using NIST SRM2724b. A description of each of the samples and spikes used in this comparison is given in Table 1.

Table 1

Samples and spikes used in this comparison of methods (uncertainties are expanded ($k = 2$))

Sample ID	Description	Nominal or certified sulfur content ($\mu\text{g g}^{-1}$)
LGC3021	Candidate diesel reference material	10
LGC3022	Candidate diesel reference material	30
LGC3023	Candidate diesel reference material	50
BCR-672	Certified gas oil reference material	203 ± 6
SRM3154	Certified reference material (sulfuric acid)	10300 ± 30
MOS	Dilution of NIST SRM3154	104.00 ± 0.21
IRMM-646	Reference material enriched in ^{34}S	161.47 ± 0.88
BAM-spike	Solution enriched in ^{34}S	99.46 ± 0.38
SRM2724b	Certified diesel reference material	426.5 ± 5.7

3.2. LGC microwave digestion and ICP-MS method

3.2.1. Reagents for MW digestion

Samples were digested using analytical grade nitric acid (Romil, Cambridge, UK). After digestion they were diluted using deionised water (18 M Ω) taken from an Elga Maxima water purification unit (Elga, Marlow, UK). NIST SRM3154 was used to correct the observed ratio of $^{32}\text{S}/^{34}\text{S}$ in the sample blends for mass discrimination. The isotopically enriched sulfur used for isotope dilution was elemental sulfur obtained from Oak Ridge Laboratories (Oak Ridge, Tennessee, USA) enriched in ^{34}S (95%). The sulfur was fully oxidised to H_2SO_4 in concentrated HNO_3 using the closed vessel microwave technique outlined in detail below. The concentration of this spike was determined by reverse isotope dilution mass spectrometry using a gravimetrically prepared standard from NIST SRM3154.

3.2.2. Procedure for microwave digestion followed by ICP-MS measurement

Sample digestion of the study samples was performed using the Multiwave 2000 microwave oven (Anton Paar, Austria). Details of the microwave program are given in Table 2. After digestion, the samples were diluted with deionised water to a minimum final weight of 20 g.

In addition, the next generation microwave, the Multiwave 3000 (Anton Paar, Austria), was used to prepare digestions of the NIST SRM2724b. This allowed a higher maximum pressure of 80 bar and a higher maximum temperature of 260 °C.

Table 2

Microwave digestion conditions

Sample weight	0.1 g
Digestion acids	5 ml HNO_3 + 0.8 ml H_2O_2
Maximum temp	200 °C
Maximum pressure	75 bar
Microwave settings: stage 1	Ramp from 50 to 1000 W over 15 min
Microwave settings: stage 2	Hold at maximum temp for 30 min

Download English Version:

<https://daneshyari.com/en/article/10528933>

Download Persian Version:

<https://daneshyari.com/article/10528933>

[Daneshyari.com](https://daneshyari.com)