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Development of a Species-Unspecific Isotope Dilution GC−ICPMS Method for Possible Routine Quantification of Sulfur Species in Petroleum Products

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Inductively coupled plasma mass spectrometry (ICPMS) hyphenated with capillary gas chromatography was applied for sulfur multispecies determination in petroleum products by species-unspecific isotope dilution mass spectrometry (IDMS). To guarantee a stable and continuous addition of the spike into the GC−ICPMS system, a special dosing unit was designed and synthesis of a ^{34}S-labeled dimethyldisulfide spike from ^{34}S-enriched elemental sulfur in the milligram range was developed. The sample was mixed with an internal standard for spike mass flow calibration. From the mass flow chromatogram obtained by species-unspecific GC−ICP-IDMS, determination of all separated sulfur species and of the total sulfur content was possible without any matrix influence by coeluting hydrocarbons. The accuracy of the developed method was evaluated by determining reference material SRM-2296 certified for three sulfur species and by comparison of results obtained by species-specific GC−ICP-IDMS. The total sulfur concentration determined for all separated species agreed well with the sulfur content in the original samples which demonstrated that all sulfur species have been covered. Structural characterization of sulfur species was carried out by corresponding sulfur standards and by applying electron ionization ion trap mass spectrometry. The low detection limit of 9 ng sulfur per gram sample, independent of results on coeluting hydrocarbons, and the robust instrumental design of the continuous spike flow dosing unit qualifies this species-unspecific GC−ICP-IDMS method for accurate and sensitive sulfur multispecies determinations also on a routine basis.

Because of the growing concerns toward the hazardous influence of sulfur compounds released by the combustion of sulfur containing fuels, the legal limit of sulfur in gasoline and diesel fuel has been lowered constantly during the last years.[1,2] For example, this limit was reduced for gasoline in the EU in 2005 from 150 to 50 μg/g. Even now "sulfur-free" gasoline with sulfur contents of less than 10 μg/g is already available. These low sulfur concentrations necessitate sensitive, fast, and accurate analytical methods for total sulfur determination. Direct injection of the sample into an ICPMS allows sensitive and fast analyses of sulfur and other trace elements as it was recently demonstrated for biodiesel applying a reaction/collision cell quadrupole ICPMS.[3] In addition, matrix-independent accuracy can be achieved by the use of the isotope dilution technique. This was demonstrated by injection of a microemulsion of an aqueous spike solution in the organic phase of the sample or by laser ablation of a sample mixed with a ^{34}S-labeled organic spike compound, respectively.[4,5] Also for optimization of the refinery process, an accurate quantitative determination of sulfur species at the different technical steps is necessary on a routine basis.[6] This is due to the different reactivity of the species in the desulfurization step.[7] In addition, fingerprints of sulfur species in crude oil and petroleum products can be used for the exploration of oil fields[8,9] or for the investigation of environmental contamination sources.[10,11] The systematic numbering of the substitution positions of thiophene, benzothiophene, and dibenzothiophene is shown in the formulas on the next page. Hyphenated techniques by coupling gas chromatography with an atom emission or a chemiluminescence detector have been used in the past for quantification of sulfur species.[12,13] Detection limits of only 50−500 ng sulfur/g could be achieved with such detection

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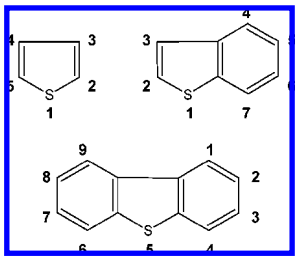

methods. A significant improvement was the use of GC−ICPMS systems where detection limits in the range of 0.5−10 ng/g could be reached.[14−16] However, the excellent detection limits of GC−ICPMS hyphenated techniques do not avoid matrix influences on the sulfur signal by the high amount of hydrocarbons in petroleum products. A matrix-independent detection and calibration method would therefore substantially simplify quantification of sulfur species and also guarantee highly accurate results.

Isotope dilution mass spectrometry (IDMS) is internationally well-known as a highly accurate analytical method and accepted as a "primary method of measurements". The GC−ICP-IDMS technique for elemental species can be carried out in a species-specific or species-unspecific spiking mode.[17] In the case of the species-specific spiking mode, the isotope-labeled spike, which must be identical in its chemical form with the analyte, is mixed with the sample at the very beginning. This has the advantage that possible loss of substance during the following separation step has no effect on the result in contrast to the species-unspecific spiking mode where the spike addition is carried out after separation of the different elemental species (postcolumn spiking). One big disadvantage of the species-specific spiking mode, especially for multispecies determinations on a routine basis, is the required use of individual spike compounds for all species of interest whereas the species-unspecific spiking mode only needs a single spike compound in any chemical form.

Recently, a species-specific GC−ICP-IDMS method was developed for three main sulfur species in gasoline and diesel fuel.[18] This method is especially useful for highly accurate determinations of corresponding sulfur species in standards and reference materials or for validation of other analytical techniques. The aim of the present work was the development of a species-unspecific GC−ICP-IDMS method for accurate and sensitive sulfur multispecies quantification. A suitable ^{34}S-labeled spike compound for the species-unspecific technique was therefore synthesized and a system for postcolumn introduction of a stable spike flow into the GC separated sulfur species was established. Structural information was obtained by retention time comparison with corresponding standard compounds in combination with GC−EI-MS (EI, electron ionization) analyses using ion trap mass spectrometry.

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EXPERIMENTAL SECTION

Chemicals and Samples. The following sulfur species of natural isotopic composition with certified purities in the range of 96−99.5% were used as laboratory standards: thiophene, 2-methylthiophene, 2-ethylthiophene, benzothiophene, dibenzothiophene, 2-methyldibenzothiophene, 4-methyldibenzothiophene, and 4,6-dimethyldibenzothiophene (Acros Organics, Belgium, or Aldrich-Chemie, Germany). Additional sulfur standard compounds in toluene were provided by J. T. Andersson (Institute of Inorganic and Analytical Chemisty of the University of Münster, Germany). The GC carrier gas helium was of 5.0 purification grade and the argon plasma gas of 4.8 purification grade. Methyllithium in diethylether (1.6 mol/L) and iodine with 99.8% purity (Acros Organics) were applied for synthesis of the dimethyldisulfide spike, and *n*-hexane (Fluka, Switzerland) was used for the preparation of internal standard solutions and for dilution of samples. ^{34}S-isotope enriched elemental sulfur was purchased from Eurisotop (Saint-Aubin, France).

The following reference materials, only certified for total sulfur, were analyzed: two vacuum gas oil samples (BCR 107 and BCR 672) with certified sulfur contents of 10 400 ± 150 and 203 ± 6 μg/g, respectively, one gasoline sample (ERM-EF211), and one "sulfur-free" gasoline (ERM-EF213) with certified values of 48.8 ± 1.7 and 9.1 ± 0.8 μg/g (Institute for Reference Materials and Measurements IRMM, Geel, Belgium). A standard reference material (synthetic gasoline SRM-2296; National Institute of Standards and Technology NIST, Gaithersburg, MD), certified for three sulfur compounds (thiophene 31.0 ± 1.0 μg/g, 3-methylthiophene 36 ± 1 μg/g, benzothiophene 69 ± 1 μg/g), was analyzed for method validation. In addition, sulfur speciation was also carried out for one diesel fuel from a gasoline station, naphtha obtained from a refinery (MIRO, Karlsruhe, Germany), and a heating oil sample from a household tank.

All samples and standards were stored in airtight glass vessels at −20 °C until they were used. Plastic vessels must be avoided because substantial adsorption and possibly also diffusion of the lipophilic compounds into the plastic material can cause significant changes of concentration with time.

GC−ICPMS Hyphenated System for Species-Unspecific Isotope Dilution Analysis. Capillary gas chromatography was coupled with quadrupole ICPMS (model HP 4500, Agilent Technologies, Wilmington, DE). The isotope-diluted sample was separated by capillary GC (gas chromatograph HP 6890, Agilent Technologies) using a 60 m long dimethylpolysiloxane column (Zebron ZB1, Phenomenex, Torrance, CA; column diameter 0.32 mm; stationary phase 1 μm). The helium gas flow was 1.6 mL/min, and the temperature program was always adapted to a sufficient separation of sulfur species in the different samples (Table 1). About 1 μL of the sample, when an internal standard has been added, was injected for GC separation by applying a split ratio of 3:1 to 50:1 depending on the sulfur species concentration. Samples with high sulfur concentrations were typically measured at split ratios of 50:1.

Coupling of the gas chromatograph with the torch of the ICPMS was arranged by a self-made directly heated transfer line and a connection unit, which have recently been described in detail.[18] At the GC side, the separation capillary is directly coupled to the transfer line by a Swagelok screwed joint. At the ICPMS

Table 1. GC Temperature Programs Used for Sample Analysis by Species-Unspecific GC−ICP-IDMS

sample	temperature program
synthetic gasoline (SRM-2296)	50 °C (2 min) → 250 °C (20 °C/min, 4 min)
gasoline (ERM-EF 211)	40 °C (2 min) → 180 °C (6 °C/min) → 340 °C (30 °C/min, 4 min)
"sulfur-free" gasoline (ERM-EF 213)	40 °C (2 min) → 180 °C (6 °C/min, 4 min)
naphtha	40 °C → 60 °C (6 °C/min, 1 min) → 240 °C (7 °C/min) → 300 °C (20 °C/min, 4 min)
vacuum gas oils (BCR 107 and BCR 672), heating oil, diesel fuel	50 °C (2 min) → 150 °C (20 °C/min, 2 min) → 320 °C (8 °C/min, 4 min)

side, the transfer line is first led through a self-made glass adapter and ends in the plasma torch. The glass adapter and the plasma torch are connected by a spherical joint, which enables easy movement of the torch position. To avoid cold spots, which would lead to condensation of high-boiling compounds, the transfer line is heated. The end-position of the transfer line in the plasma torch, which was about 1.8 cm in front of the load coil in this investigation, is relatively critical with respect to signal intensity and peak width of chromatograms. The optimum ICPMS measurement conditions were 700 W rf power at argon gas flows of 15.5, 0.8, and 1.25 L/min for the cooling, auxiliary, and carrier gases, respectively. Sulfur isotope ratio measurements by a quadrupole ICPMS can have severe interference with oxygen contaminants. The argon plasma gas was identified to be the major source of oxygen contamination, which could substantially be reduced by a gas purification system (ALO-750-4, Rainer Lammertz Pure Gas Products, Hürth, Germany). The remaining low oxygen background did not influence the measurements by species-unspecific GC−ICP-IDMS.

A continuous and stable "postcolumn" flow of the ^{34}S-labeled dimethyldisulfide spike was generated by coupling a gas cylinder under pressure with the inlet for the carrier gas at the glass adapter via a two-stage valve and an electronic flow controller (MKS PR 4000; MKS Instruments, Wilmington, MA). The total amount of synthesized spike compound, stored in a glass tube and covered with a plug, was introduced into a 10 L argon steel gas cylinder. Argon was added into the cylinder until a total pressure of about 7000 kPa was reached. By shaking of the cylinder, the glass tube was opened and the spike compound was mixed with the argon gas. After a couple of hours, to allow equilibration between argon and the liquid spike compound, the gas cylinder could be used for postcolumn spiking. The corresponding spike flow rate was fixed at about 1 mL/min, and the spike mass flow was calibrated by the use of an internal standard added to the sample (see section on species-unspecific isotope dilution technique). A constant spike mass flow was always observed over a couple of hours.

Identification of Sulfur Species. Because species-unspecific GC−ICP-IDMS can only be used for quantification of sulfur species, for identification other analytical methods must be applied. A simple method is to follow the signal enhancement of separated peaks after addition of corresponding standard compounds. Such an identification method is convenient in cases where only a few sulfur species appear in the chromatogram and where coelution of different species can be excluded. With respect to the complexity of most samples analyzed in this work, this technique could only be used as preliminary information so the electron ionization ion trap mass spectrometer (PolarisQ Ion Trap GC/MSn, Thermo Fisher Scientific, Bremen, Germany) was applied to obtain more reliable structural information. Because of the relatively low fragmentation of the aromatic sulfur compounds by electron ionization (70 eV), sulfur species were mostly characterized by their molecular mass. Whereas species with relatively high concentrations were measured in the scanning mode (mass range 50−290 u; 3 scans/s), the more sensitive selected ion mode (target mass ±0.5 u; 4 scans/s) was applied for low-abundance sulfur species. In cases where identification was not possible after EI-MS measurements, MS/MS experiments were added. However, in some cases it was not possible to differentiate between coeluting isomers like 2-methyl- and 3-methyldibenzothiophene by these mass spectrometric methods.

Synthesis of Dimethyldisulfide Spike. The spike compound was selected by its chemical and physical stability and that it must produce a sufficiently high and stable spike mass flow from the gas cylinder under pressure. In addition, synthesis from ^{34}S-enriched elemental sulfur at the milligram level should be relatively simple. Under these requirements, dimethyldisulfide was selected and its synthesis was realized by the following two-step reaction:

$$CH_3Li + {}^{34}S \rightarrow H_3C-{}^{34}SLi \xrightarrow[-LiI]{+I_2} H_3C-{}^{34}S-{}^{34}S-CH_3 \qquad (1)$$

An amount of 200 mg of ^{34}S-enriched elemental sulfur was dried under vacuum conditions in a microflask. Under an argon atmosphere, 8 mL of methyllithium in diethylether was added so that the corresponding lithium salt of methylsulfide was formed. After stirring a couple of hours to complete the first reaction step of eq 1, elemental iodine was carefully added until a consistent color was observed. The main fraction of diethylether was then evaporated on a water bath at about 50 °C, and the concentrated solution was again stirred for a couple of hours. Afterward, a fractionated distillation was carried out on an oil bath, first at 80 °C for 1.5 h to eliminate the forerun, followed by the product fraction of dimethyldisulfide distilled at a temperature range of 95−135 °C. This main fraction was separated from residues of diethylether by heating at 80 °C. The reaction yield related to the original ^{34}S-enriched material was 45%. Identity and purity of the spike compound was confirmed by ^{1}H NMR spectroscopy and sulfur analysis by GC−ICPMS. ICPMS resulted in a ^{34}S-enrichment of 99.3% (by 0.6% of ^{32}S and 0.1% of ^{33}S). The relevant spike isotopic composition during species-unspecific GC−ICP-IDMS analyses is always slightly different from the original spike material due to small sulfur contaminations with natural isotopic composition, preferably from the gas cylinder and the argon plasma gas. However, this has no influence on the results because the actual isotope ratio of the spike is always measured during chromatographic separation of samples. For example, the constant isotope ratio in the beginning of the isotope-diluted BCR 107 chromatogram (up to a retention time of about 15 min in Figure 1b) represents the relevant spike isotope ratio because this section of the chromatogram is free of eluted sulfur compounds with the exception of the internal standard.

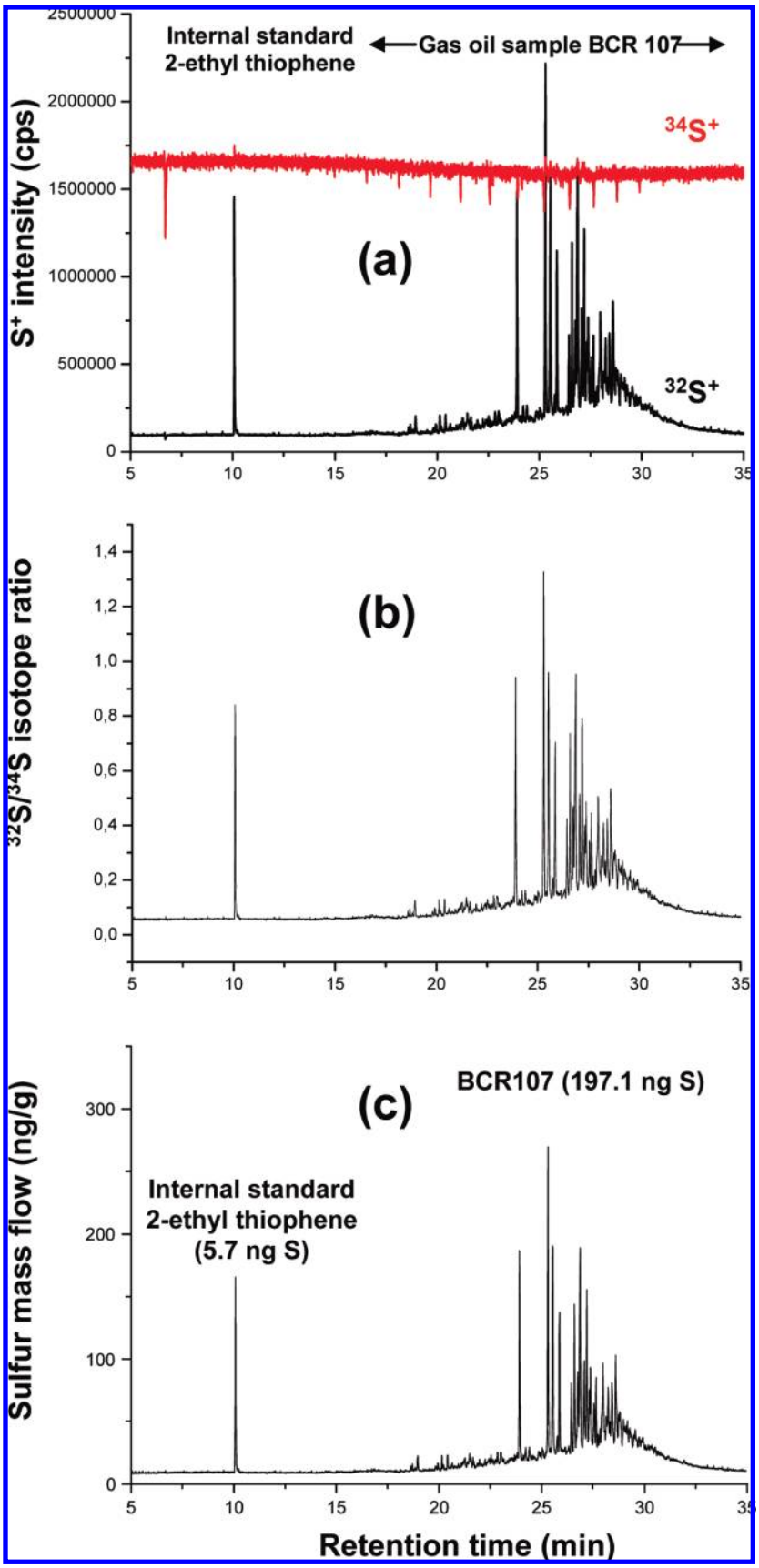

Figure 1. Analytical procedure for the determination of sulfur species by species-unspecific GC−ICP-IDMS with internal standardization demonstrated by the example of vacuum gas oil BCR 107. (a) Measured ion intensity chromatogram of the isotope-diluted sample (negative peaks in the $^{34}S^+$ track are caused by solvent *n*-hexane and coeluting main fractions of hydrocarbons; the slightly decreasing $^{34}S^+$ intensity along the chromatogram is caused by changing plasma conditions during introduction of the sample); (b) calculated isotope ratio chromatogram $^{32}S/^{34}S$; (c) calculated sulfur mass flow chromatogram by using the internal standard for calibration.

Table 2. Determination of Sulfur Species in Vacuum Gas Oil BCR 107 by Species-Unspecific GC−ICP-IDMS

species	species concentration (μg/g)	species concentration (μg sulfur/g)
2,7-dimethylbenzothiophene	47.0 ± 2.3	10.1 ± 0.5
2,4-dimethylbenzothiophene	80.6 ± 2.6	17.3 ± 0.7
2,3-dimethylbenzothiophene	244 ± 4	52.5 ± 0.8
2,4,7-trimethylbenzothiophene	434 ± 13	85.3 ± 2,6
dibenzothiophene and naphtho[1,2-b]thiophene (coelution)	1300 ± 52	226 ± 9
4-methyldibenzothiophene	2239 ± 87	362 ± 14
2- and 3-methyldibenzothiophene (coelution)	1986 ± 68	321 ± 11
1-methyldibenzothiophene	1108 ± 43	179 ± 7
4,6-dimethyldibenzothiophene	1172 ± 40	177 ± 6
1,4-dimethyldibenzothiophene	1504 ± 39	227 ± 6
2,4,6-trimethyldibenzothiophene	1306 ± 42	185 ± 6
sulfur content of identified species		1842
total sulfur content by GC−ICP-IDMS		10501 ± 67
total sulfur content certified		10400 ± 150
fraction of quantified species		17.7%

An alternative to the use of dimethyldisulfide are alkylthioethers, which also fulfill the necessary requirements for spike compounds. Preliminary investigations with sulfur of natural isotopic composition have shown that syntheses of diethylthioether and dipropylthioether in the milligram range can be carried out with a little higher reaction yields of 50−62% compared to dimethyldisulfide.

Species-Unspecific GC−ICP-IDMS with Internal Standard for Spike Mass Flow Calibration. From the fundamental equation for isotope dilution mass spectrometry[19,20] one can calculate the amount m_S of sulfur in a sample. GC separation causes a time-dependent mass flow of the sulfur species $Mf_S(t)$ which also results in a time-dependent isotope ratio R(t) of the isotope-diluted sample. On the other hand, the mass flow of the spike Mf_{Sp} remains constant over the whole chromatogram. With measurement of R(t) along the peak of a separated sulfur species, the time-dependent mass flow $Mf_S(t)$ is obtained. Integration within the retention time limits t_1 and t_2 of a separated sulfur species results in the total amount m_S of this separated species

$$m_S = \int_{t1}^{t2} Mf_S(t)\, dt = Mf_{Sp}\frac{M_S}{M_{Sp}}\int_{t1}^{t2}\frac{{}^{34}h_{Sp} - R(t)\,{}^{32}h_{Sp}}{R(t)\,{}^{32}h_S - {}^{34}h_S}\, dt \qquad (2)$$

with M_S and M_{Sp} as the atomic weight of the sample and spike, respectively, and h_S and h_{Sp} the corresponding sulfur isotope abundances.

To calculate the sulfur amount of separated species by eq 2, the exact spike mass flow must be known. Direct and accurate determinations of gaseous mass flows are relatively difficult. To eliminate this problem, an exactly weighed amount of an internal standard of natural isotopic composition in *n*-hexane was always added to the sample. To avoid coelution, a sulfur compound different in its retention time to those in the sample was selected for standardization. For determinations of sulfur species in low-boiling petroleum products, dibenzothiophene was therefore applied whereas in the case of analyzing high-boiling sulfur species 2-ethylthiophene was used.

For the known amount of internal standard m_{Std} in the gas chromatogram, an analogous equation as for m_S is valid. Equation 2 directly correlates with the peak area A_S of the elemental species to be determined in the sulfur mass flow chromatogram which is also true for the corresponding equation of m_{Std}. By dividing eq 2 by the corresponding equation for m_{Std}, the following simple relation between the amount of sulfur in a separated species and the amount of internal standard is obtained

$$m_S = m_{Std}\frac{A_S}{A_{Std}} \qquad (3)$$

under the assumption that M_s is identical with M_{Std}. The maximum relative error caused by this assumption is less than 0.04% and was calculated using the range of atomic weights in natural occurring sulfur compounds reported by IUPAC.[21]

Equation 3 shows that the sulfur amount of species can be determined without any knowledge of the spike mass flow by only determining the peak areas of the internal standard and the corresponding sulfur species assuming an arbitrary spike mass flow. A precondition for this internal standardization is there are no discriminations between the analyzed species and the internal standard. This was approved by determining recoveries of a synthetic standard mixture of sulfur species of different volatility in the range of applied split ratios.

For analyses by species-unspecific GC−ICP-IDMS, about 1 g of the internal standard solution in *n*-hexane (concentration is adapted to the corresponding amount of sulfur in the sample) and about 1 g of the sample, both exactly weighed, are mixed. Under these conditions the uncertainty by weighing is negligible. On the other hand, only 1 μL of this mixture is injected into the GC which is not as easy for an exact dosage. Thus, the additional big advantage of the use of an internal standard is the fact that

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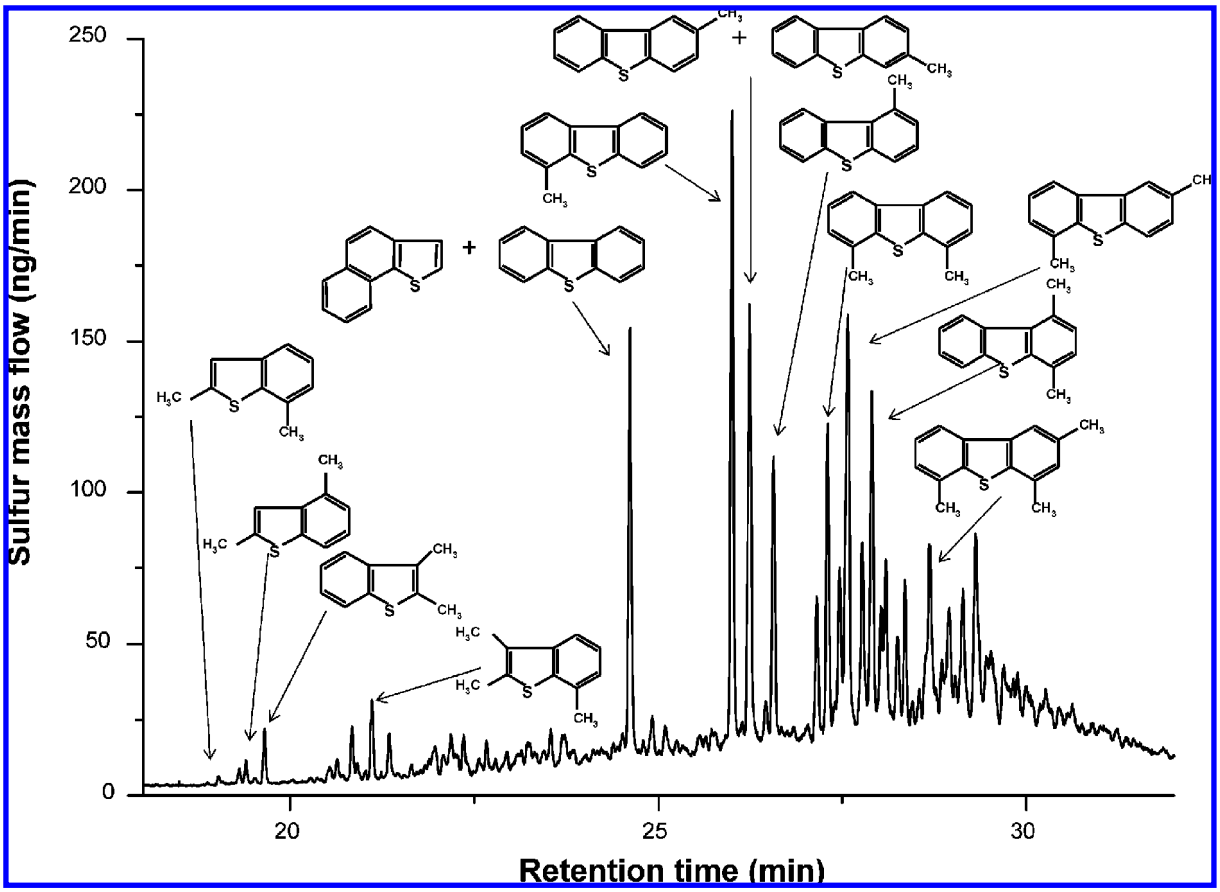

Figure 2. Sulfur mass flow chromatogram of vacuum gas oil sample BCR 107 with identified sulfur species by EI-MS.

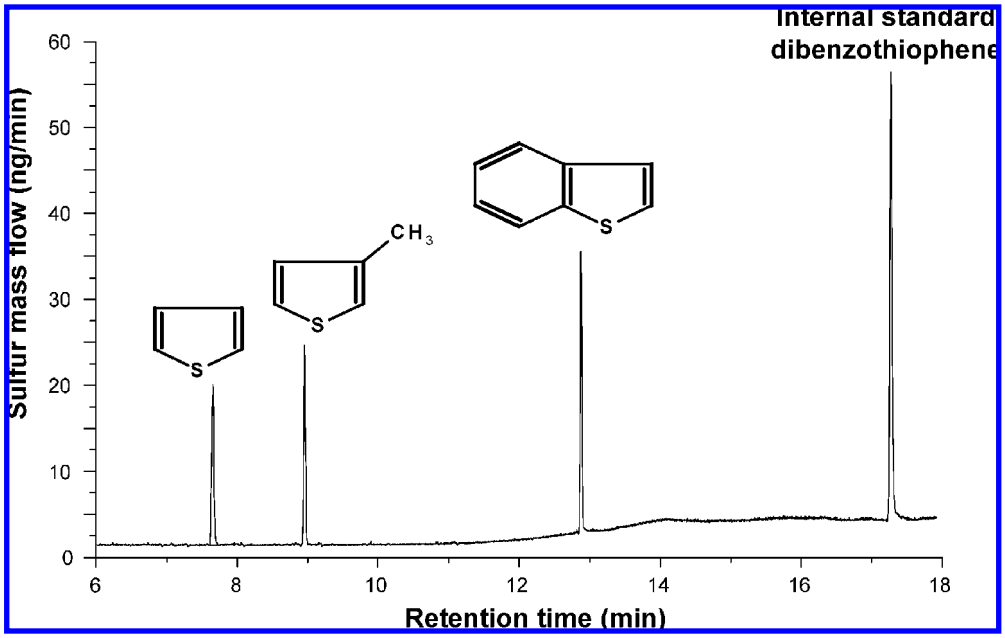

Figure 3. Sulfur mass flow chromatogram of standard reference material SRM-2296 containing three certified sulfur species.

uncertainties in the injection volume do not have any influence on the analytical result because the determined ratio A_S/A_{Std} is independent of the injected volume of this mixture. Only the spike mass flow must be stable during detection of the corresponding chromatogram which was always fulfilled by the designed spike generation unit.

However, for calibration of the sulfur mass flow of the sample (*y*-axis of Figure 1c) the spike mass flow must be determined. An arbitrary value Mf'_{Sp} is therefore estimated for the spike mass flow which results in a virtual amount of internal standard m'_{Std} given by the following equation integrated within the corresponding time limits t_3 and t_4:

$$m'_{\mathrm{Std}} = \mathrm{Mf'}_{\mathrm{Sp}} \frac{M_{\mathrm{S}}}{M_{\mathrm{Sp}}} \int_{t3}^{t4} \frac{{}^{34}h_{\mathrm{Sp}} - R(t)\,{}^{32}h_{\mathrm{Sp}}}{R(t)\,{}^{32}h_{\mathrm{Std}} - {}^{34}h_{\mathrm{Std}}}\,\mathrm{d}t \qquad (4)$$

If the corresponding equation for m_{Std} is divided by eq 4, the following simple correlation is obtained because the integrals and atomic weights in these equations are cancelled:

$$\mathrm{Mf}_{\mathrm{Sp}} = \mathrm{Mf'}_{\mathrm{Sp}} \frac{m_{\mathrm{Std}}}{m'_{\mathrm{Std}}} \qquad (5)$$

Because the injected amount of the internal standard m_{Std} is known, the real mass flow of the spike can easily be calculated by eq 5.

RESULTS AND DISCUSSION

Species-Unspecific GC−ICP-IDMS with Internal Standardization for Sulfur Speciation. The principles of the species-unspecific ICP-IDMS technique were developed for the first time in 1994 by coupling HPLC with ICPMS.[22] Compared to the species-specific isotope dilution mode, it has the advantage that only one isotope-labeled spike is necessary for multispecies determinations, which is especially important due to the great number of different sulfur species usually present in petroleum products. By application of the species-unspecific technique it is also possible to quantify unknown elemental species. Both isotope dilution modes are time-efficient due to their internal calibration, and in addition, real-time concentrations of separated elemental species are received which is not possible with other analytical methods. To obtain accurate results, it must be guaranteed in the species-unspecific mode, in contrast to the species-specific one, that loss of analyte does not occur until the postcolumn isotope dilution step has taken place. To prove this precondition, the total amount of sulfur in the original sample was always compared with the sum of all sulfur species detected in the chromatogram.

One important precondition for accurate analyses by GC−ICP-IDMS is a constant spike mass flow. One possibility to generate such constant mass flows is the use of a permeation tube. However, this technique is extremely sensitive to temperature variations and also not very flexible with respect to the generated rate of substance. A steel gas cylinder, filled under pressure with argon and a sufficiently volatile spike compound, was therefore applied in this work as a spike reservoir from where a constant spike mass flow could be generated by the two-stage valve and the electronic flow controller. This also allowed flexible adjustment of the spike flow with respect to an optimization of the analyte/spike ratio for IDMS analyses.[19] Under constant spike mass flow conditions during detection of a sulfur mass flow chromatogram, calculation of the amount of separated species became relatively simple because only the ratio of peak areas of the different sulfur species in relation to that one of the internal standard must be evaluated (see eq 3). Mass bias corrections for isotope ratio measurements are also not necessary due to the fact that the corresponding peak areas are measured under exactly identical conditions. In addition, the use of an internal sulfur standard of natural isotopic composition in the sample enables accurate determination of the spike mass flow during detection of each individual chromatogram. Linear response of the ICPMS was observed in the measured concentration ranges measured, which is an important precondition for internal standardization. All these advantages implement a high power of species-unspecific GC−ICP-IDMS with internal standardization to be used as an accurate, fast, and sensitive routine method for sulfur multispecies determinations in petroleum products.

Table 3. Determination of Sulfur Species in the Certified Standard Reference Material SRM-2296

species	certified value (μg/g)	species-unspecific GC−ICP-IDMS (μg/g)
thiophene	31 ± 1	31.2 ± 0.3
3-methylthiophene	36 ± 1	35.9 ± 0.6
benzothiophene	69 ± 1	69.0 ± 0.4
total sulfur content	40.0 ± 0.4	40.1 ± 0.7

Figure 1 demonstrates the experimental procedure for quantitative sulfur multispecies determination by species-unspecific GC−ICP-IDMS with internal standardization using the analysis of vacuum gas oil BCR 107 as an example. The first analytical step is the detection of the ion intensities of the spike and reference isotope ($^{34}S^+$ and $^{32}S^+$) with dependence on the retention time of the gas chromatographic separation (Figure 1a). Second, the $^{32}S/^{34}S$ isotope ratio chromatogram is calculated (Figure 1b) from the results presented in Figure 1a. The third analytical step is quantification of the different sulfur species by their peak areas in comparison to the peak area of the internal standard by applying eq 3. Calibration of the mass flow axis can be carried out according to eq 5. Quantitative results for 13 major sulfur species in gas oil sample BCR 107, obtained by this analytical procedure after structural characterization, are listed in Table 2. The fourth analytical step is always to check if the sum of all sulfur species in the chromatogram covers the sulfur content of the original sample or if any loss occurred during separation. Hence, the mass flow of all sulfur species associated with sample BCR 107 was integrated which resulted in a total amount of 197.1 ng of sulfur (see Figure 1c). By the known amount of sample injected into the GC, this value corresponds to a total sulfur content of 10 501 ± 67 μg/g (mean with standard deviation obtained by three parallel chromatograms of this sample) which excellently agrees with the certified value of 10 400 ± 150 μg/g (Table 2) and also confirms that loss of sulfur species did not occur during GC separation.

Structural information of major sulfur species of gas oil sample BCR 107 is presented in Figure 2, which is an extended chromatogram in the high-retention time section of Figure 1c. Table 2 summarizes the concentrations of all identified sulfur species. In the case of coeluting species, the given concentration is the sum of these species. This is true for dibenzothiophene and naphtho[1,2-b]thiophene, on the one hand, and for 2-methyl- and 3-methyldibenzothiophene, on the other. 2,6-Dimethyldibenzothiophene is also indicated in Figure 2, but the corresponding concentration is not listed in Table 2 because coelution with an unidentified compound took place. For sample BCR 107, only 17.7% of all sulfur species were identified even if the most abundant species are among them. This clearly

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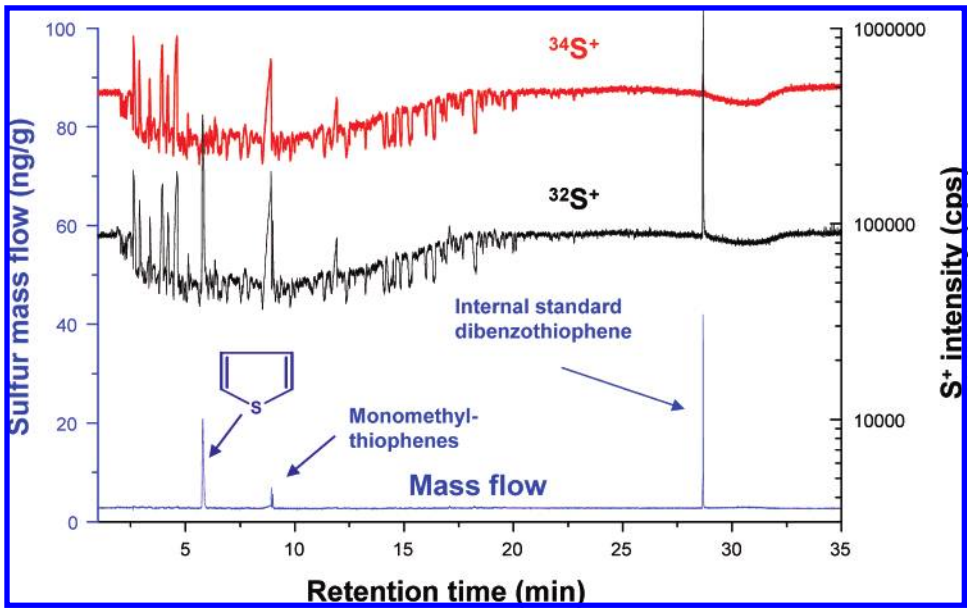

Figure 4. Measured sulfur ion intensity chromatogram (split ratio 3:1) of "sulfur-free" gasoline ERM-EF 213 demonstrating the influence of the hydrocarbon matrix at retention time interval of 2−21 min and representation of the matrix-independent sulfur mass flow chromatogram by GC−ICP-IDMS.

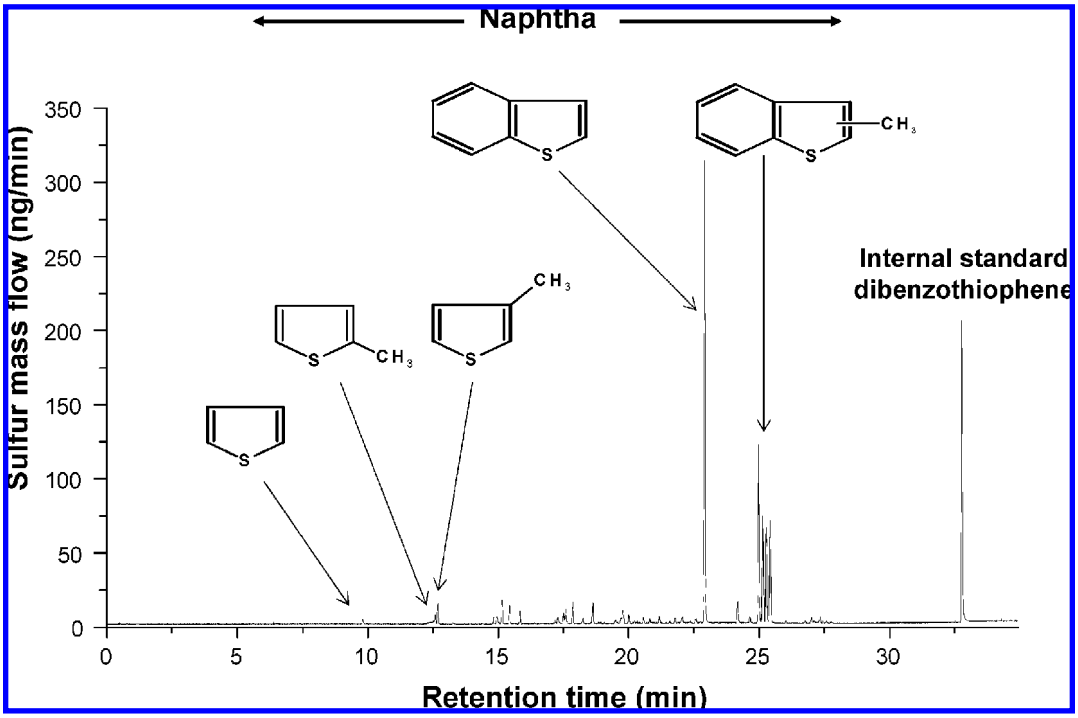

Figure 5. Sulfur mass flow chromatogram of the naphtha sample with identified sulfur species.

demonstrates the complex character especially of high-boiling petroleum products.

Validation of Species-Unspecific GC−ICP-IDMS. Because of a lack of "real world" reference materials, a synthetic standard reference material (SRM-2296), certified for three sulfur species, was analyzed for validation of the method. The corresponding sulfur mass flow chromatogram is shown in Figure 3 where dibenzothiophene was used as an internal standard. From this mass flow chromatogram, the results listed in Table 3 were obtained which excellently agree with the certified values of all three sulfur species but also with the certified total sulfur content.

Even if an excellent agreement between the certified and species-unspecific GC−ICP-IDMS data exists for sample SM-2296, it was not known if possible matrix effects in real samples can influence the accuracy of results or not. The high amount of hydrocarbons in petroleum products usually substantially influences the ion intensity of sulfur as was clearly demonstrated in a recent publication[18] but also by the results represented in Figure 4. The $^{34}S^+$ and $^{32}S^+$ signal intensities of a chromatogram of the "sulfur-free" gasoline sample ERM-EF 213 are plotted while a continuous and stable postcolumn spike flow is introduced into the system. Hydrocarbons are simultaneously eluted with the

Table 4. Determination of Major Sulfur Species in Three Low-Boiling Petroleum Products ("Sulfur-Free" Gasoline ERM-EF 213, Gasoline ERM-EF 211, Naphtha) by Species-Unspecific GC−ICP-IDMS

	concentration (μg sulfur/g)		
species	"sulfur-free" gasoline	gasoline	naphtha
thiophene	6.62 ± 0.12	5.67 ± 0.12	3.08 ± 0.07
monomethylthiophenes	1.33 ± 0.09[a]	4.77 ± 0.07[a]	18.5 ± 1.2[a]
benzothiophene		1.66 ± 0.04	280 ± 2
monomethylbenzothiophenes		1.67 ± 0.08[a]	328 ± 5[a]
dibenzothiophene and naphtho[1,2-b]thiophene		0.25 ± 0.02[a]	
4-methyldibenzothiophene		0.14 ± 0.01	
2- and 3-methyldibenzothiophene		0.18 ± 0.01	
1-methyldibenzothiophene		0.27 ± 0.01	
sulfur content of identified species	7.95	14.61	629.6
total sulfur content by GC−ICP-IDMS	9.50 ± 0.04	46.2 ± 2.1	914 ± 20
total sulfur content certified or by direct injection ICP-IDMS[b]	9.1 ± 0.8	48.8 ± 1.7	939 ± 20[b]
fraction of quantified species	84.4%	29.9%	67.1%

[a] Sum of coeluted isomeric sulfur species. [b] Total sulfur content determined by direct injection ICP-IDMS.

Table 5. Determination of Major Sulfur Species in Three High-Boiling Petroleum Products (Vacuum Gas Oil, Diesel Fuel, Heating Oil) by Species-Unspecific GC−ICP-IDMS

	concentration (μg sulfur/g)		
species	gas oil BCR 672	diesel fuel	heating oil
benzothiophene			7.6 ± 0.3
monomethylbenzothiophenes	1.12 ± 0.09[a]	14.4 ± 0.4[a]	15.2 ± 0.7[a]
trimethylbenzothiophenes			56.6 ± 1.6[a]
dibenzothiophene and naphtho[1,2-b]thiophene		0.58 ± 0.07	29.0 ± 0.9
4-methyldibenzothiophene	13.5 ± 0.3	2.42 ± 0.07	46.6 ± 1.4
dimethyl- and monoethyldibenzothiophenes		9.72 ± 0.24[a]	45.8 ± 1.6[a]
2- and 3-methyldibenzothiophene	0.35 ± 0.09	0.47 ± 0.05	28.1 ± 0.8
1-methyldibenzothiophene		0.28 ± 0.01	14.4 ± 0.5
4,6-dimethyldibenzothiophene	27.8 ± 0.6	15.9 ± 0.5	30.7 ± 0.9
1,4-dimethyldibenzothiophene	5.52 ± 0.18	1.97 ± 0.04	21.3 ± 0.6
2,4,6-trimethyldibenzothiophene	12.2 ± 0.3	7.53 ± 0.10	20.3 ± 0.7
sulfur content of identified species	60.47	53.1	315.6
total sulfur content by GC−ICP-IDMS	200 ± 10	185 ± 8	1575 ± 65
total sulfur content certified or by direct injection ICP-IDMS[b]	203 ± 6	174 ± 4[b]	1587 ± 49[b]
fraction of quantified species	29.8%	30.5%	19.9%

[a] Sum of coeluted isomeric sulfur species. [b] Total sulfur content determined by direct injection ICP-IDMS.

sulfur species in the retention time interval of 2−21 min. In this section of the chromatogram, both sulfur isotopes are significantly influenced by the hydrocarbon matrix which causes clearly detectable peaks (positive and negative ones due to an enhancement or depression of signal intensity) even at retention times where no sulfur species are present. However, both sulfur isotopes are influenced in the same way so that the corresponding isotope ratio and, thus, the sulfur mass flow was not influenced which can be seen from the corresponding chromatogram in Figure 4. The strong influence on the accuracy of results by coelution of hydrocarbons in sample ERM-EF 213 becomes obvious by analyzing thiophene without the isotope dilution technique but using GC−ICPMS with internal calibration by dibenzothiophene. Whereas the species-unspecific GC−ICP-IDMS method resulted in 17.4 ± 0.3 μg of thiophene per gram sample, the result for GC−ICPMS with internal standardization was only 9.4 ± 0.3 μg/g. This disagreement is due to the fact that thiophene but not the internal standard dibenzothiophene was influenced by light hydrocarbons in the case of the latter method. The detection limit of the species-unspecific GC−ICP-IDMS was calculated from the mass flow chromatogram of Figure 4 to be 9 ng of sulfur by 3 times the standard deviation at retention times without sulfur species elution.

The species-specific isotope dilution technique can be, in general, classified at a higher level of accuracy compared to the species-unspecific method due to some additional limitations of the species-unspecific mode (possible loss of analyte until post-column spiking and possible species discrimination by the ICPMS introduction system[17]). For validation of the species-unspecific technique, comparison with results of species-specific GC−ICP-IDMS are therefore also convenient. The thiophene content of the "sulfur-free" gasoline sample ERM-EF 213 was determined to be 17.2 ± 0.2 μg/g by the species-specific method[18] which agrees very well with the above listed result for species-unspecific GC−ICP-IDMS. Corresponding thiophene results for the naphtha sample are 8.3 ± 0.2 and 8.1 ± 0.2 μg/g, using the sulfur mass flow chromatogram of Figure 5 for calculation of the species-unspecific value. 4-Methyldibenzothiophene in heating oil was determined to be 289 ± 10 and 288 ± 9 μg/g by the species-

specific and species-unspecific method, respectively, as an example for the analysis of high-boiling sulfur species.

Sulfur Multispecies Determinations by Species-Unspecific GC−ICP-IDMS in Different Low- and High-Boiling Petroleum Products. To demonstrate the broad application range of the developed method, different low-boiling and high-boiling petroleum products were analyzed for their sulfur species. Table 2 contains the complete set of identified sulfur species for vacuum gas oil sample BCR 107. For better comparison between the individual species, the species concentration was not only presented in micrograms of species per gram but also in micrograms of sulfur per gram of sample. In Tables 4 and 5, the corresponding results for three different low-boiling and three high-boiling petroleum products are listed. So far as reference materials have been analyzed, the certified total sulfur content was used to calculate the fraction of sulfur of all identified species, in the case of noncertified materials, the sulfur content determined by direct injection ICP-IDMS[23] was applied (last line of Tables 2, 4, and 5). This fraction varies strongly from 17.7% to 84.4% depending on the type of sample.

Comparison of total sulfur contents (third line from bottom of Tables 2, 4, and 5) with the total certified or directly determined sulfur concentration of corresponding samples showed good agreement in all cases within the limits of error. Thus, it can be followed that all sulfur species of the original samples have been detected so that any inaccuracy by loss of substance can be excluded.

CONCLUSION

Species-unspecific GC−ICP-IDMS enables accurate quantification of all sulfur species in low-boiling but also high-boiling petroleum products. Structural information of the different sulfur species can be obtained by electron ionization ion trap mass spectrometry and MS/MS analyses. Only a single ^{34}S-labeled spike compound is necessary for sulfur multispecies determinations. The developed design for generating a continuous spike flow is a robust and stable system. Besides the accuracy of the results, additional advantages of the species-unspecific GC−ICP-IDMS are matrix-independent and time-effective measurements as well as real-time quantifications. The additional use of an internal standardization causes simple sample handling and an easy evaluation of results by adequate calibration of the spike mass flow. All these advantages predestine the developed method for accurate, sensitive, and fast sulfur multispecies determinations on a routine basis. In addition, multispecies determinations should also be possible for other elements by species-unspecific GC−ICP-IDMS using analogous principles as described in this work. Because of the fact that the species-unspecific GC−ICP-IDMS method is especially effective and advantageous for simultaneous multispecies determinations, corresponding analyses of silicon, selenium, germanium, chlorine, and bromine may be of interest in the future.

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