Available online at www.sciencedirect.com
SCIENCE DIRECT®

Talanta 69 (2006) 776–780

Talanta

www.elsevier.com/locate/talanta

Determination of sulfur content of diesel fuels and diesel fuel-like fractions of waste polymer cracking

N. Miskolczi [a,*], L. Bartha [a], J. Borszéki [b], P. Halmos [c]

[a] *Department of Hydrocarbon and Coal Processing, University of Veszprém, Egyetem u. 10 Veszprém, H-8200, Hungary*
[b] *Department of Analytical Chemistry, University of Veszprém, Hungary*
[c] *University of Veszprém, Research Group for Analytical Chemistry of the Hungarian Academy of Science, Hungary*

Received 16 June 2005; received in revised form 26 October 2005; accepted 7 November 2005
Available online 5 December 2005

Abstract

The element content of low and high sulfur containing diesel fuels was measured by different analytical methods: energy-dispersive X-ray fluorescent (EDXRF) and inductively coupled plasma atomic emission (ICP-OES) spectroscopy methods. Then results were compared. High sulfur containing diesel fuels were from heavy diesel engines and diesel fuel-like liquids obtained by thermal degradation of waste polymers. In case of X-ray analysis also the effect of the used thin foils with different chemical compositions (polypropylene, polycarbonate, polyester) on the accuracy was investigated. According to data considerable differences and deterioration of accuracy was observed in the respect of foils in case of both low and high sulfur containing hydrocarbons. Results indicated appropriate correlation between experimental results measured by both two methods, but differences could be observed in the correlation, which could be explained with different ratio of C/H of samples.

Keywords: Energy dispersive X-ray fluorescence spectroscopy; Inductively coupled plasma atomic emission spectroscopy; Sulfur content; Waste plastic degradation

1. Introduction

The concentration of sulfur and its proper determination play an important role regarding fuels and products of petrochemical industry. The problem of appropriate determination of sulfur is important both from environmental and analytical aspects, because some specifications order to the compulsion decrease of the concentration of sulfur (e.g. from 2005 their maximum concentration is 50 mg/kg in fuels in the countries of European Union) [1–3]. Furthermore the reduction of sulfur content generates further analytical problems. On one hand, the development of hydrodesulfurazition processes was quicker than that of qualification standardized methods and instruments. On the other hand, at present there are great ambitions to create the harmony between different methods [4,5].

It is not left out of consideration that there are some part of industrial area, where diesel oils with high sulfur content are allowed and used (e.g. heavy special diesel engines). It means that a suitable technique for the determination of sulfur content in fuels has to possess measuring ability for the analyte in a wide range of concentrations (from the unit of ppm to %). There are numerous spectroscopic techniques to analyze the qualitative and quantitative elemental composition of fuels and lubricants: inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectroscopy (ICP-MS), flame or graphic furnace atomic absorption spectroscopy (AAS) or by X-ray fluorescent spectrometry (XRFS) [5–14]. Each technique has advantageous properties in terms of analytical figures of merit. The atomic absorption and emission techniques are typically used for analysis of the products of hydrocarbon industry. The ICP technique is a fast analytical method, but needs preliminary sample preparation (e.g. digestion). Whereas the energy dispersive X-ray fluorescent spectrometry is a non-destructive, furthermore cost-effective method of elemental analysis of the samples. According to our experience an ideal analytical technique has to posses quick and easy sample preparation, sample homogeneity, simultaneous multi-element detection capability and naturally appropriate precision, repeatability and reproducibility. Application of EDXRFS to determine the sulfur content of hydrocarbon mix-

---

[*] Corresponding author. Tel.: +36 88 423 225; fax: +36 88 423 225.
E-mail address: mnorbert@almos.vein.hu (N. Miskolczi).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.11.006

tures obtained by cracking of waste polymers is a new route of analysis.

Nowadays both the consumption and the production of plastics is increasing by 4–5% annually. According to data, the amount of plastic waste was more than 30 Mt only in the European region. The increasing consumption of plastic materials and their wastes could generate considerable environmental problems, because their suitable handling is an also unsolved problem. This is one reason of others that there are numerous ambitions to stimulate the development of recycling and reusing processes of waste polymers. Because of the high rate of their application polyethylene, polypropylene and polystyrene are mainly investigated. These polymers may be subjected to cracking methods where the long carbon chain of polymer are cracked into lighter hydrocarbons with shorter chains, giving a mixture of hydrocarbon gases, liquids and heavier products [15–21]. One possible way for the utilization of products issued from polymer cracking is the application as fuels. The main advantage of such fuel-like fractions is the low sulfur content.

In this work, we studied comparatively the results of different analytical techniques (EDXRFS and ICP-OES) for the assay of commercial high sulfur containing diesel fuels from heavy engines and liquids obtained by thermal cracking of waste polymers.

2. Experimental

2.1. Samples

Diesel fuels with high sulfur content of diesel current generator from Paks Nuclear Power Plant (Hungary) (from the mark of DS-1 to DS-13), and liquid fractions of batch cracking process of waste polymers (polyethylene (CS-1) and mixture of polyethylene and polystyrene (CS-2)) were used. The degradation of plastic waste was carried out in a horizontal tube reactor, which was described in our previous publication [22]. The cracking equipment consisted of three main parts: an extruder, a reactor and a separator. The preheated polymer was driven from the extruder into the reactor, where the polymers were melted and cracked into lighter fragments. These fractions were separated by atmospheric and vacuum distillation to naphtha, diesel fuel, light and heavy oils. The liquid products of the cracking reactions were analyzed by a gas chromatograph and by infrared analysis (SHIMADZU IR-470 Infrared Spectrophotometer). Table 1 shows the main properties of samples.

Table 2
EDXRFS operating conditions

Target	S Ka line
Detector	Si-PIN
Foil	Polycarbonate, polypropylene, polyester
Voltage	6 kV
Current	300 μA
Filter	None
Medium	Helium
Measure time	180 s

According to data significant differences were observed among commercial and experimental samples. Commercial diesel fuels contained only paraffins, olefins and napthens, whereas diesel fuel-like fraction obtained by the cracking of high-density polyethylene and polystyrene contained also aromatics (CS-2).

2.2. Instruments and sample preparation

2.2.1. PHILIPS MiniPal PW 4025/02 energy dispersive X-ray spectrometer

For measurements a non-polarized energy dispersive X-ray fluorescent spectrometer (PHILIPS MiniPal PW 4025/02) was used. The spectrometer powered by PW 4051 MiniPal/MiniMate Software V 2.0A and the software also features an integrated deconvolution function that separates closely spaced peaks in the spectrum that the system would otherwise be unable to resolve. The spectrometer was equipped with a 9 W Rh-side window tube anode and Si-PIN detector. The anode angle was 90° with respect to the central ray. The fluorescent X-rays were detected with a Si-PIN detector with beryllium window, and the raw signal was counted with a counter fitted with 2048 channel. The special de Kat sample holder and thin films (polycarbonate, polypropylene and polyester) were obtained from Philips Analytical B.V. The operating conditions for this experiment are summarized in Table 2. Samples did not need pre-treatment in this case. The part of sample holder was put together and filled with sample then it was analyzed.

2.2.2. GBC Integra XM type ICP spectrometer

The sulphur determination was carried out with a GBC Integra XM type ICP-OES spectrometer (Australia) (Table 3). After performing the background equivalent concentration experiment

Table 1
The main properties of measured liquid fractions

Sample	Density, g/cm^3	*M*, g/mol	Paraffin, %	Olefin, %	Naphten, %	Aromatic, %
DS-1	0.829	224.8	46.1	21.0	32.8	-
DS-2	0.840	216.4	51.5	23.7	24.8	-
DS-3	0.839	225.9	49.6	24.8	25.6	-
DS-4	0.843	219.4	51.5	25.8	22.7	-
DS-5	0.839	220.4	46.1	21.5	32.4	-
DS-6	0.839	227.7	51.5	24.8	23.7	-
CS-1	0.808	234.1	53.7	46.3	-	-
CS-2	0.801	225.9	39.8	36.7	-	23.5

Table 3
The properties of ICP-OES spectrometer

Type	GBC Integra XM, sequential
Nebulizer	Concentric, with a cyclonic spray chamber
RF-generator	40.68 MHz crystal-controlled
Power	1200 W
Reflected power	20 W
Obsevation high	6 mm above the coil
Optical system	Czerny-Turner vacuum-monochromator
Grating	Holographic, 1800 groves/mm
Focal length	0.75 m
Optical range	160–800 nm
Resolution	1st order: 0.018 nm
Detector	Photomultiplier
Emission lines used for the S analysis	$\lambda_1 = 180.731$ nm $\lambda_2 = 182.034$ nm

to test the instrument sensitivity, the ICP operating conditions applied are presented in Table 3.

2.2.3. *High-pressure asher*

The sample preparation for the ICP analysis was made by the high-pressure asher (HPA, Austria) device. 0.2–0.4 g of samples were weighed into the vessels. After addition of concentrated nitric acid the decomposition temperature program was run ($T_1 = 120\,°$C,0 $t_1 = 60$ min; $T_2 = 220\,°$C, $t_2 = 90$ min). After cooling down, the contents of the vessels were washed into volumetric flasks and the volume adjusted to the mark with deionised water.

3. Results

It is necessary to select a suitable analytical line by the measure of elemental concentration of samples with X-ray method. In case of this experiment, the K_a line of sulfur was used. Series of five sulfur-containing standard samples in diesel oil matrix were used to establish a calibration graph in the concentration range of 0–1000ppm. In case of EDXRFS the concentration of samples was calculated from measured raw intensities and the intensities of relevant analytical lines were corrected for the background intensity employing the MiniPal/MiniMate Software V 2.0A, which applied an α-correction method. The linearity of calibration graphs was obtained with analysis of linear regression coefficients. According to results high regression coefficient (>0.99) and no bias was observed in case of both methods.

X-ray spectrometry is one of the typical analytical methods, which needs a special sample holder. Generally, the applied sample holders are made from high purity polymers and colorless window (or foils) made from also plastics (polypropylene, polyester and polycarbonate). In order to determine the effect of the generally applied foils on the results, the concentration of sulfur in different diesel fuels and diesel-like hydrocarbons were determined. In case of the calibration process polypropylene foils was used. The aim of our work was the investigation of the differences, caused by the origin of the used other foils (polyester and polycarbonate). The sulfur content of liquids measured with different analytical methods is shown in Table 4.

Table 4
Concentration of sulfur in samples measured by EDXRFS using different foils

Foil	EDXRFS			ICP-OES
	Polypropylene	Polyester	Polycarbonate	
DS-1	874 ± 2	984 ± 5	624 ± 3	843 ± 11
DS-2	1127.5 ± 0.9	1497 ± 4	874 ± 3	1220 ± 14
DS-3	1139 ± 2	1544 ± 4	693 ± 3	1180 ± 13
DS-4	1022 ± 1	1241 ± 3	751 ± 3	1075 ± 14
DS-5	2191.5 ± 0.9	2501 ± 3	1841 ± 3	2250 ± 11
DS-6	1524 ± 1	1862 ± 5	1094 ± 3	1584 ± 13
CS-1	23 ± 2	298 ± 8	−5 ± 3	30 ± 6
CS-2	21 ± 1	305 ± 6	−5 ± 3	17 ± 4

Eight samples were measured by different methods. The results were graphically analyzed. Fig. 1 shows the comparison between two analytical methods using different foils. As shown, significant differences were found among the used foils (<8% in case of high concentration of sulfur) and the lowest difference between two techniques was observed in case of polypropylene foil. According to data of Table 4 the correlation was significantly worst in case of two other foils (polyester and polycarbonate). This phenomenon might be attributed to the elemental composition of foils. Polymers made from both polyester and polycarbonate foils contain oxygen, because of their chemical structure. The oxygen as individual element was not detectable by the used EDXRFS apparatus, but it could likely influence the analysis. The primary electron ray from the anode tube excited the electrons also on the internal electron orbital of oxygen atom. While began vacancy supplement with other electrons from internal orbital generated X-ray photons. These photons influenced mainly the background radiation and perhaps affected slightly the characteristic radiation of sulfur.

According to data of Fig. 1 the difference between EDXRFS (using polypropylene foils) and ICP-OES methods was in the range 2.3–18.8% relating to the results of the EDXRFS method. The deviations in case of ICP-OES were considerably higher than for the EDXRFS technique. It is well known that samples need to be digested in case of optical emission spectroscopy, while X-ray technique is a non-destructive method. The digestion is another possibility of errors.

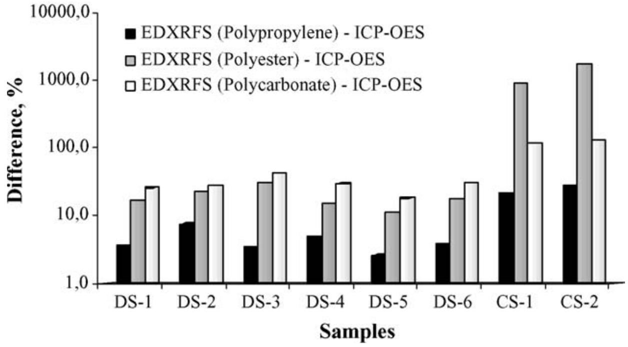

Fig. 1. Sulfur content of hydrocarbons measured by different methods.

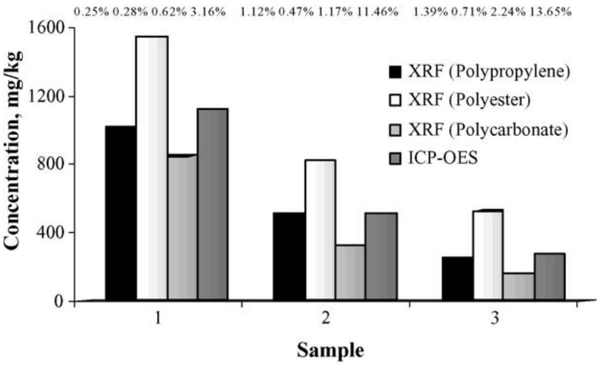

Fig. 2. Sulfur content of validated standards measured by different methods.

Not only the foils but also the chemical composition of samples affected the correlation between different methods. The matrix effect may significantly affect the accuracy in case of X-ray method. Bacaud et al. investigated the effect of C/H ratio on the concentration of sulfur in case of diesel oil. It was found that the ratio of C/H significantly affected the determination of sulfur, because increasing C/H ratio the apparent sulfur concentration is increased [15]. The matrix of the used standards in this experiment was diesel oil, which contains mainly aliphatic hydrocarbons. According to data of Table 1 CS-2 had 23.5% aromatic and only 49.3% paraffin content. Both CS-1 and CS-2 contained nearly 50% of unsaturated compounds. The correlation between the two above-mentioned methods was the best in case of DS-5 and the worst that of CS-2 sample. This is attributed to the greater ratio of C/H in case of CS-2.

Validated sulfur containing standards in diesel oil matrix was also measured by both analytical techniques. A standard ($c = 1.019$ g/kg) was obtained from the Institute for Reference Materials and Measurements, Belgium (EF 104 sample no. 0018). The standard also was diluted with sulfur free diesel oil. The standard in its original concentration (1019.0 mg/kg) and the two other diluted samples (509.0 and 248.9 mg/kg) were measured by both EDXRFS and ICP-OES methods. Fig. 2 shows the results of measurements. According to results considerable differences were observed regarding foils in case of EDXRFS method measuring validated standards. The best correlation between two methods was observed in the case of polypropylene foil. The accuracy for analysis of sulfur was much better for XRF (R.S.D. = 0.25–2.24%) than for ICP-OES (R.S.D. = 3.16–13.65%).

The correlation between the two analytical methods was followed by the t-test. The critical value of t using three independent measurements is 5.841 in case of 99% acceptance reliability level. It was found that the correlation coefficient was 0.998 and the value of t was 17.609, which is significantly higher, than the critical value. It means that there was no significant difference between the two analytical methods in the determination of sulfur content of hydrocarbons.

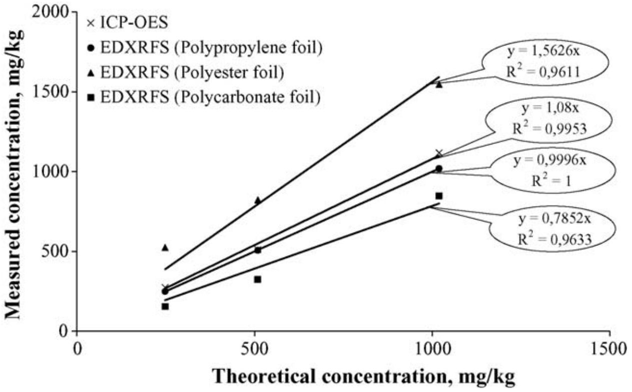

Fig. 3. Relation between theoretical and measured concentrations.

Theoretical and measured data were graphically analyzed based on the plotting of their results on x–y plots (Fig. 3). The theoretical and measured concentrations were in agreement in case when the slope of linear regression was 1. Based on the slope value, it was found that the result was the best in case of XRF technique using polypropylene foil. The cause of better correlation in case of EDXRFS than ICP-OES probably was the consequence of difference of sample preparations. EDXRFS technique is a non-destructive analytical method requiring no sample preparation, whereas samples had to be digested in case of ICP-OES analysis.

4. Conclusion

The determination of the concentration of sulfur in the products of petroleum industry is in a focus nowadays, and there are some standards to validate the results. Both of the different X-ray techniques and optical emission spectroscopy are wide spread methods for the determination of sulfur content. Two analytical methods for the determination of sulfur concentration were compared: an EDXRFS and an ICP-OES method. Moreover, the effect of the foils used in the sample holder in case of EDXRFS and the ratio of C/H on the accuracy was investigated. It was found that the foils of sample holders had a significant effect on the correlation of results between the two analytical methods. The highest differences were observed in case of polycarbonate foil. The cause of this phenomenon was attributed to the composition of foils. The sulfur content of fraction obtained by thermal cracking of plastic wastes was easily and reproducible measured by EDXRFS method. On the other hand, the effect of the hydrocarbon matrix is not negligible in this case.

Acknowledgements

The authors are grateful to the Chemical Engineering Institute's Cooperative Research Center of the University of Veszprém, and MOL Hungarian Oil and Gas Ltd. for financial support received for this work. Special thanks to Roland Nagy for technical help.

References

[1] EN 590:2000.
[2] EN 590:2005.
[3] Round Robin 2001, Report, CEN TC19 WG27.
[4] S. Pessayre, R. Bacaud, C. Geantet, M. Vriant, Fuel 78 (1999) 857.

[5] J.K. Vilhunen, A. von Bohlen, M. Schmeling, R. Klockenkamper, D. Klockow, Spectrochim. Acta Part B (1997) 953.

[6] R.D. Luggar, M.J. Key, E.J. Morton, W.B. Gilboy, Nucl. Instr. Meth. Phys. Res. A 422 (1999) 938.

[7] A. Zararsiz, R. Kirmaz, P. Arikan, Nucl. Instr. Meth. Phys. Res. B 108 (1996) 385.

[8] Z. Yang, X. Hou, B.T. Jones, Talanta 59 (2003) 673.

[9] X.O. Siyanbola, A.Y. Fasasi, I.I. Funtua, O.M. Afolabi, T.A. Adesiyan, A.R. Adetungi, Nucl. Instr. Meth. Phys. Res. B: Beam Interact. Mater. Atoms 215 (1–2) (2004) 240.

[10] U. Kramar, J. Geochem. Explor. 58 (1997) 73.

[11] X. Ding, J. Xie, Y. He, Q. Pan, Y. Yan, Talanta 53 (2000) 17.

[12] T. Ernst, R. Popp, R. van Eldik, Talanta 53 (2000) 347.

[13] M. Pouzar, T. Černohorský, A. Krecjčová, Talanta 54 (2001) 829.

[14] N. Chen, W. Liu, Mater. Res. Bull. 36 (2001) 137.

[15] J.L. Ferrero, C. Roldan, M. Ardid, E. Navarro, Nucl. Instr. Meth. Phys. Res. A 422 (1999) 868.

[16] M. Necemer, P. Kump, M. Rajcevic, R. Jacimovic, B. Budic, M. Ponikvar, Spectrochim. Acta Part B 58 (2003) 1367.

[17] M. Hemmerlin, J.M. Merment, M. Bertucci, P. Zydowicz, Spectrochim. Acta Part B 52 (1997) 421.

[18] A. Marucco, Nucl. Instr. Meth. Phys. Res. B 213 (2004) 486.

[19] J. Mellawati, M. Sumarti, Y. Menry, S. Surtipanti, P. Kump, Appl. Radiat. Isotopes 54 (2001) 881.

[20] T. Ernst, R. Popp, R. van Eldik, Talanta 53 (2000) 347.

[21] N. Ekinci, Y. Kurucu, E. Öz, Y. Sahin, Radiat. Measurements 35 (2002) 223.

[22] N. Miskolczi, L. Bartha, G. Deák, B. Jóver, Polym. Degrad. Stability 86 (2004) 357.