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Talanta 66 (2005) 1264–1271
Talanta
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Determination of sulphur in liquids obtained by thermal cracking of waste polymers and commercial fuels with different analytical methods

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Received 27 September 2004; received in revised form 16 January 2005; accepted 21 January 2005
Available online 26 February 2005

Abstract

Low sulphur concentration in hydrocarbon products as fuels or lubricants is an important requirement for the high quality standards of refineries. A non-polarised energy dispersive X-ray fluorescence spectroscopy (EDXRFS) and sample combustion technique (ASTM D6428-99) was compared. A new application of energy dispersive X-ray spectrometry as analytical method for the determination of sulphur in fuels and fuel-like fractions was investigated. Low sulphur containing fuels and hydrocarbon mixtures obtained by thermal cracking of waste polymers were measured and the influence of C/H ratio on accuracy was studied. The concentration of sulphur in samples was measured with calibration graphs of different hydrocarbon matrices (commercial gasoline, diesel oil and white oil were used). Good correlation was observed between the different methods, but the correlation was depending on the characteristics of the matrices. Detection limits of 1.0 ppm, 1.1 ppm and 0.9 ppm were obtained for S in gasoline, diesel oil and white oil, respectively.

Keywords: Energy dispersive X-ray fluorescence spectroscopy; Sulphur concentration; Waste plastic; Thermal cracking; Matrix effect

1. Introduction

Recycling and reusing of waste plastics has been of great interest in terms of the solution of their environmental and economic problems. Therefore, the utilization of a huge amount of waste plastic has been in the focus of investigations for the last 15 years. Plastic consumption was 150 Mt in 2000 worldwide, and it is estimated to be 258 Mt in 2010 [1,2]. Not only the plastic consumption is growing, but also the amount of wastes from them. In 2010, plastic consumption will be 75 Mt and the wastes 40 Mt only in Europe [1–3]. Nowadays, the utilization of the growing mass of wastes is an unsolved problem. Basically, there are four ways for its solution: landfilling, mechanical recycling, chemical recycling and incineration. Plastic waste incineration and landfilling are not the most desirable ways for the utilization of the growing amounts of plastic wastes due to the high cost of suitable depos and the possibility of the emission of harmful compounds (e.g. SO_X, NO_X, CO, CO_2, dioxins, dust, etc.). On the other hand, recently some directives were introduced by the EU for reducing the ratio of landfilling and fostering recycling and reusing [2]. By chemical recycling (cracking) the long carbon chain of polymers can be degraded into lighter hydrocarbon fragments. The degradation of waste polymers results in hydrocarbon gases, liquids and residue. Under suitable degradation conditions the main fraction might be the liquid. The further utilization routes of liquids obtained by cracking of waste plastics are aimed at by researchers [4–9]. One obvious possibility of their further utilization is that as fuel, because liquids consist of gasoline and diesel oil. Mainly polyethylene, polypropylene

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doi:10.1016/j.talanta.2005.01.041

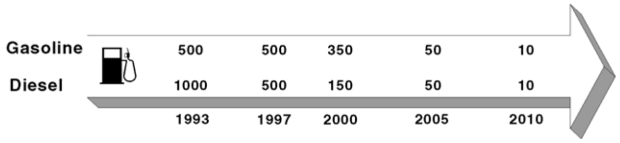

Fig. 1. The change of sulphur concentration.

and polystyrene constitute the basis of degradation because they have no heteroatom content therefore, the products of the degradation are theoretically free of sulphur. As a matter of fact these fractions always contained a low amount of sulphur. This fact may be attributed to the antifire and smoke reductant additives with sulphur content in the extruded polymers, which might accumulate in liquids obtained by the thermal degradation of wastes.

On the other hand, there is a tendency to reduce the sulphur content in fuels and motor oils. Nowadays, the maximum concentration of sulphur in gasoline is 150 ppm, and in diesel oil is 350 ppm in the European Union [10,11]. From 2005 in countries of the EU the maximum concentration of sulphur will be reduced both in gasoline (50 ppm) and diesel oil (150 ppm). In all probability after 2010 only sulphur free fuels will be able to get on the market. In Fig. 1 the change of the sulphur concentration in gasoline and diesel oil in Hungary is shown from 1993 till now.

The concentration of sulphur both in gasoline and diesel oil significantly decreased from 1993 to 2000, and in accordance with EU directives it will have to be further decreased till 2010. The above mentioned concentration of sulphur and the production of sulphur free fuels can be almost achieved with the new generation of hydrodesulphurization catalysts in the petroleum refining industry. The problem is rather analytical, and new standards have to be initiated because of the low concentrations. There are some well known methods for the determination of the sulphur content of fuels: microcoulometry, energy or wavelength dispersive X-ray fluorescent spectroscopy (XRFS) [12–16]. The energy dispersive X-ray fluorescent spectroscopy is a non-destructive cost-effective method of the elemental analysis of samples. The ideal analysis technique has to posses quick and easy sample preparation, sample homogeneity, simultaneous multi-element detection and appropriate precision, repeatability and reproducibility. On the other hand, due to the development of analytical apparatus, some new experimental method can be used in low concentration ranges. For measurements energy dispersive X-ray fluorescent spectroscopy (EDXRFS) is suitable for the determination of, e.g. sulphur in low concentration range (under 50 ppm). Furthermore, there are ambitions to harmonize the different sulphur determination standards in the EU [17].

In the present paper, the results obtained by non-polarized energy dispersive X-ray fluorescent spectroscopy and a sample combustion method (ASTM D6428-99) are compared. The possible ways for determination of sulphur concentrations in different matrices were studied. The influence of the matrix effects on the accuracy was also investigated by using liquids obtained in thermal degradation of waste polyolefins (polyethylene, polypropylene) and polystyrene.

2. Experimental

2.1. Materials

Liquid fractions of products from waste polymer degradation were used as samples. The type of degradation of wastes was a mild thermal cracking process, which was carried out in a horizontal tube reactor in the temperature range of 520–530 °C. Polyethylene, polypropylene and polystyrene were degraded. Liquids formed in the cracking reactions of waste polymers were separated into two fractions: a lighter fraction, which has properties as a white spirit, and a heavier diesel like hydrocarbon fraction. The liquid products of the cracking reactions were analysed by a gas chromatograph (TRACE GC) employing FID detector and a Chromcad

Table 1
The main properties of the liquid fractions

	Sample 1		Sample 2		Sample 3		Sample 4	
	1-G[a]	1-D[a]	2-G	2-D	3-G	3-D	4-G	4-D
Liquids obtained by thermal cracking of waste polymers								
Hydrocarbons (%)								
Linear	94.7	96.9	5.3	4.1	46.9	46.7	34.2	47.2
Branched	6.3	4.1	93.8	94.7	53.7	53.3	39.9	51.4
Aromatic	0.0	0.0	0.9	0.0	0.0	0.0	25.9	1.4
$-CH_2-/-CH_3$[b]	3.9	6.9	0.9	1,6	1,6	3,5	1,6	3,6
Boiling range (°C)	54–208	187–299	42–199	194–319	43–203	196–307	35–210	189–311
M (g/mol)	112	218	110	221	111	222	106	219
Waste polymer mixture (%)								
Polyethylene	100		–		50		50	
Polypropylene	–		100		50		40	
Polystyrene	–		–		–		10	

[a] The “G” symbol represents the lighter (gasoline-like), and the “D” the heavier (diesel-like) fraction.

[b] Number of $-CH_2-/-CH_3$ groups in average molecule (measured with infrared spectra using SHIMADZU IR-470 Infrared Spectrophotometer).

column. The branched chain structure of liquid paraffinic hydrocarbons was further confirmed by infrared analysis (SHIMADZU IR-470 Infrared Spectrophotometer). Table 1 shows the main properties of liquids obtained by thermal cracking of wastes.

The waste samples cracked in this process had principally great differences in their chemical structure. Samples 1 and 2 have only polyethylene or polypropylene content, in contrast with the other two samples, which were mixtures of polyethylene and polypropylene in case of Sample 3, and polyethylene, polypropylene and polystyrene in case of Sample 4. Because of the different composition of the raw materials, their degradation products were also different. It was found that the chemical structure of waste polymers profoundly affected the chemical composition of the cracking products. In cases of Samples 1–3 only aliphatic, linear and branched hydrocarbons were detected. The cracking of polyethylene (Sample 1) resulted in hydrocarbons with linear structure, in contrast to polypropylene (Sample 2), which has a branched polymer chain structure; therefore, the products of its cracking resulted in a high concentration of branched hydrocarbons in the liquid fraction. Sample 4 had 10% polystyrene content, which degraded mainly into benzene, toluene, ethyl-benzene and styrene. The aromatic content in these liquids formed by the cracking of Sample 4 was 25.9% in case of 4-G and 1.4% in 4-D.

In the investigation of matrix effect on the accuracy of sulphur determination the calibration curves were plotted by using different hydrocarbon products of petroleum refining industry, i.e. gasolines, diesel oils and white oil. The main properties of matrices used as standards are summarized in Table 2. Each hydrocarbon fraction had a low concentration of sulphur: 7.1 ppm, 10.9 ppm, 13.5 ppm in case of gasoline, diesel oil and white oil, respectively. The initial concentration of sulphur in various hydrocarbon products was measured by using APS 35™ elemental analyser according to the standard test method ASTM D 6428-99. This analyser was fitted with only a sulphur detector. The standard samples for calibration were prepared by dissolving dibutyl sulphide (MERCK-Schnuchardt, with a purity of 96%) in the concentration range of 0–100 ppm.

Table 2
The main properties of matrices

	Gasoline	Diesel oil	White oil
Density (g/cm^3)	0.744	0.839	0.856
S content (ppm)	7.1	10.9	13.5
M (g/mol)	135	203	264

2.2. Analytical equipment

2.2.1. APS 35™ elementary analyser (ASTM D6428-99)

ASTM D6428-99 technique and the APS 35™ elementary analyser are well known and suitable method and instrument for the determination of sulphur at a low concentration level. The detectable concentration range of the applied analyser was 300 ppb–1000 ppm. After preparation the liquid samples were put in the furnace, where its sulphur content was quantitatively converted to sulphur-dioxide. Sample combustion was carried out in a relatively pure oxygen atmosphere (99.996%) at a temperature over 1000 °C. Sulphur-dioxide was reacted on the sensing electrode in a 3-electrode electrochemical cell. This reaction produces a measurable current, which is directly proportional to the amount of sulphur in the original sample. The mathematical calculation and integration of the raw signal were made with APS 35 Elemental WorkStation™ software.

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

EDXRFS is also a well known technique for the determination of sulphur in liquid hydrocarbons. A non-polarised energy dispersive X-ray fluorescent spectrometer used in this work was a PHILIPS MiniPal PW 4025/02 spectrometer powered by PW 4051 MiniPal/MiniMate Software V 2.0A (Philips Analytical B.V., Almeno, The Netherlands). This instrument has a proprietary software, which is Windows® based. 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. This spectrometer equipped with a 9 W Rh side-window tube anode and Si-PIN detector and different filters, as molybdenum, kapton, aluminium and silver. The anode angle was 90° with respect to the central ray. Fluorescent X-rays were detected with a Si-PIN detector with beryllium window. X-ray photons were counted with a counter having 2048 channels. This X-ray instrument had a sample chamber with the possibility of holding up to 12 samples. Both the special sample holder and thin polycarbonate films were obtained from Philips Analytical B.V. The optimal instrumental operating conditions for this experiment are summarized in Table 3. The current of 350 μA and 5 kV anode voltage was used because this combination of voltage and current resulted in the highest signal to noise ratio for most samples. To reduce the photon emission of noble gases (He, Ar, Ne and Kr) from air, helium (purity of 99.996%) was used as medium.

Table 3
EDXRFS operating conditions

Target	S Ka line
Detector	Si-PIN
Foil	Polycarbonate
Voltage	5 kV
Current	350 μA
Filter	None
Medium	Helium
Measuring time	180 s

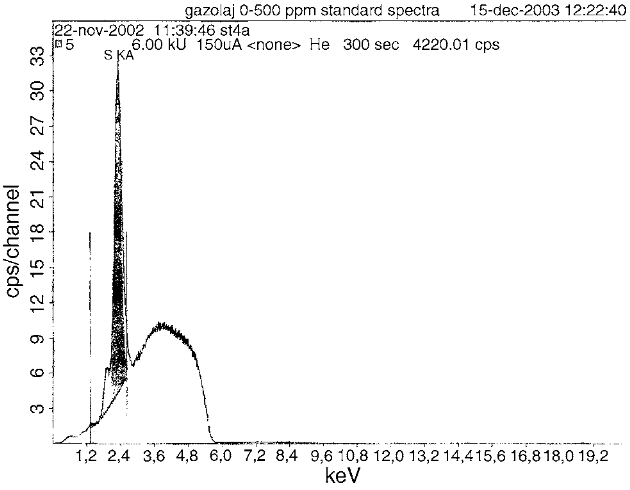

Fig. 2. The X-ray spectra of gasoline sample.

3. Results and discussion

3.1. Liquids obtained by thermal degradation of waste polymers

Fig. 2 shows the X-ray spectrum of standards from the gasoline sample. The calibration graphs were produced with a measure of seven standards in each matrix, which was prepared by dissolution of dibutyl sulphide in different hydrocarbon matrices. The calibration graph gives the relation between concentration of sulphur and the calculated fluorescent signal (Figs. 3 and 4).

Significant differences were observed between calibration graphs measured with different instruments and analytical methods. Fig. 3 indicates the calibration graphs using the sample combustion technique. No matrix effect was observed in this case. In contrast, considerable effect of the hydrocarbon matrices on the properties of calibration graphs was found when using the EDXRFS method. This is the consequence of the method. The C/H ratio is an important parameter in X-ray spectrometry, because it is based on the excitation of electrons. In general, not only the electrons of detectable atoms but also those of not detectable atoms are excited. The highest slope and therefore the greater sensitivity were observed when using standards of gasoline matrix in case of EDXRFS technique.

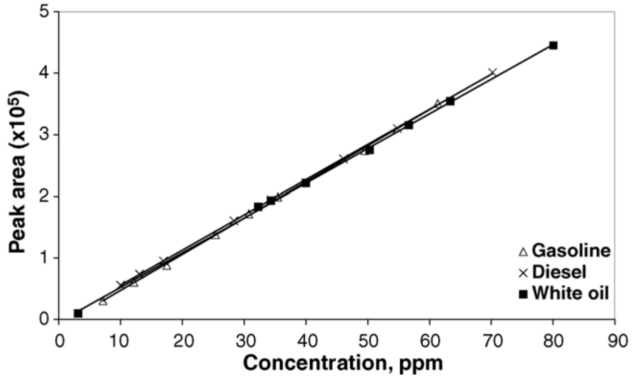

Fig. 3. Calibration graphs obtained by APS 35^{TM} instrument (ASTM D 6428-99).

$$\text{Sensitivity} = \frac{\Delta c}{\Delta S} \tag{1}$$

The sensitivity of calibration graphs was defined with Eq. (1), which indicates the change of the measured signal of instrument (ΔS) on the influence of unit change of concentration (Δc).

The linearity of calibration graphs was proved by the analysis of linear regression coefficients. They are given in Table 4. It was found, that the linear regression coefficients of the calibration graphs were higher than 0.99 in case of

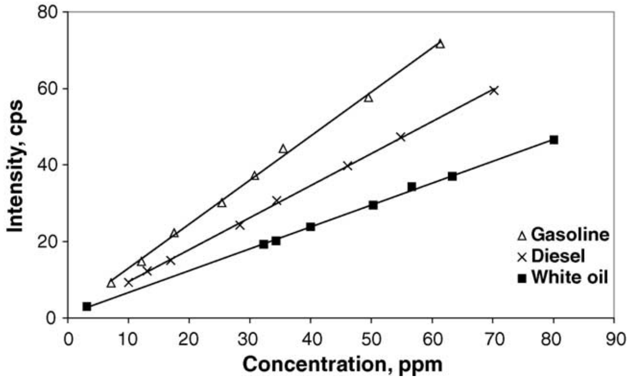

Fig. 4. Calibration graphs obtained by PHILIPS MiniPal PW 4025/02 instrument (ASTM D 6428-99).

Table 4
Properties of calibration graphs

	Method					
	Sample combustion[a]			EDXRFS[a]		
	Gasoline	Diesel	White oil	Gasoline	Diesel	White oil
Equation	$y = 5861.8x - 11123$	$y = 5660.5x - 172$	$y = 5627.6x - 3740$	$y = 1.1512x + 1.5166$	$y = 0.847x + 0.8936$	$y = 0.5712x + 0.9783$
RMS	–	–	–	1.557848	1.378358	0.217825
K-value	–	–	–	0.000433	0.000486	0.000069
R^2	0.9993	0.9999	0.9994	0.9980	0.9985	0.9990
Confidence interval	9588	6384	9173	1.9734	0.98164	0.6731

[a] Using different hydrocarbon matrices.

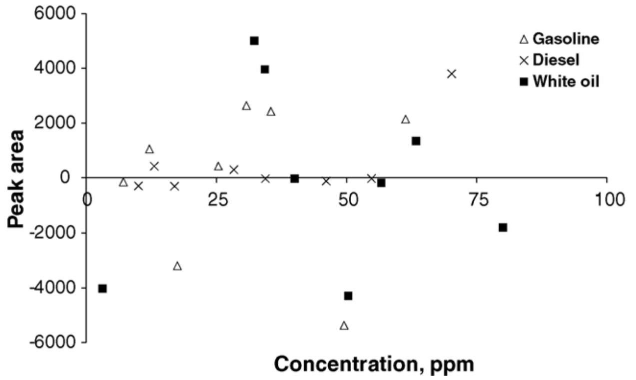

Fig. 5. Distribution of residuals measured with the sample combustion method.

each technique and set of matrices. Table 4 shows also the mathematical equation of the calibration curves and their confidence intervals. The axial intercept was always containing the zero under 95% acceptance reliability level. The value of *K*-factor and RMS were calculated by Eqs. (2) and (3).

$$K=\sqrt{\sum\left[\frac{\left(\frac{x_i}{w_i}\right)^2}{N_{\text{std}}-N_{\text{cal}}}\right]} \quad (2)$$

$$\text{RMS}=\sqrt{\sum\left[\frac{(x_i)^2}{N_{\text{std}}-N_{\text{cal}}}\right]} \quad (3)$$

By calculations the following definitions were applied. The N_{std} is the number of standard samples for the analysis, N_{cal} the number of calibration parameters being calculated for the analysis, x_i the difference between undiluted actual and calculated concentration of the analysis (%), and w_i is the error weight for analysis in standard number i defined as $w_i=[c_i+0.1]^{1/2}$, c_i is the actual concentration for the analysis in standard sample i.

The distribution of residuals was random along the *Y*-axis, therefore, there was no biased (Figs. 5 and 6).

Hydrocarbon samples obtained from thermal degradation of waste polymers (polyethylene, polypropylene, polystyrene and their mixture, see in Table 1) were measured using both two instruments and calibration curves. Results are summarized in Table 5.

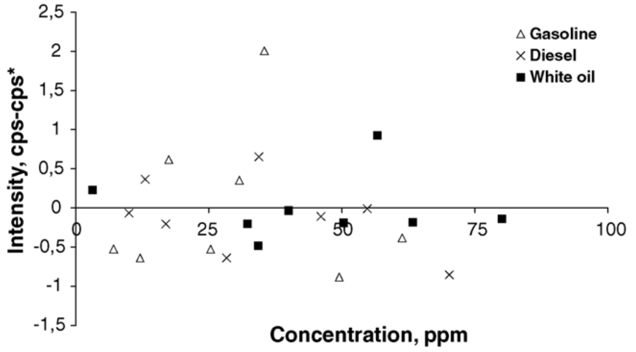

Fig. 6. Distribution of residuals measured with the EDXRFS method.

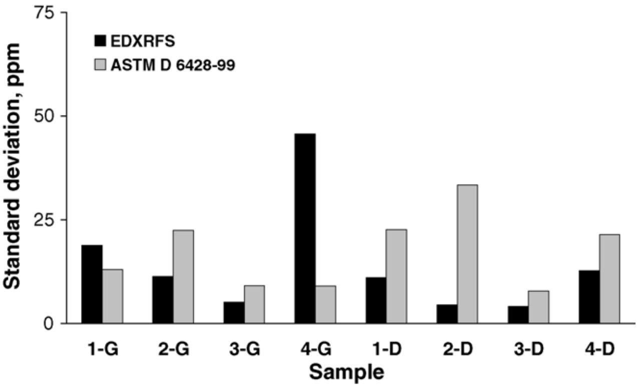

Fig. 7. The average of the concentration of sulphur using standards in gasoline matrix and different instruments.

The concentration of a given sample was determined under the same circumstances, five times successively. Both the mean and deviation of measured values were calculated. For the sake of comparison of results the standard deviation of measured values was derived with Eq. (4).

$$\text{R.S.D.\%}=\frac{\text{S.D.}}{\bar{x}_i}\times 100 \quad (4)$$

In Eq. (4) R.S.D.%, S.D. and $\bar{x}_i$ are the variation coefficient of measurement, their standard deviation and average of measurements *i*, respectively. The values of R.S.D.% are given in Table 5.

The Low Limit of Detection (LLD) gave of information about the lowest possible concentration of measure, which is detectable at a reliability of 95% level. The value of LLD was calculated with Eq. (5).

$$\text{LLD}=\text{LLD(factor)}\cdot c\cdot\sqrt{\frac{\frac{\text{Background}}{\text{MeasureTime}}}{\text{GrossPeak}-\text{Background}}} \quad (5)$$

where Background is the background intensity from the background profile (using same width) and GrossPeak is the

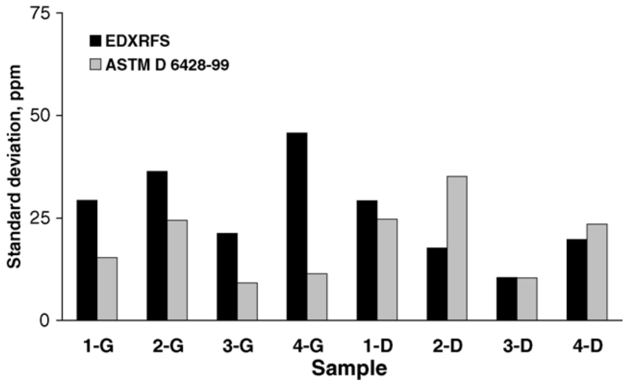

Fig. 8. The average of the concentration of sulphur using standards in diesel oil matrix and different instruments.

Table 5
Sulphur content of samples (ppm)

Instrument	Matrix	1-G[a] Gasoline	1-G[a] Diesel oil	1-G[a] White oil	2-G[a] Gasoline	2-G[a] Diesel oil	2-G[a] White oil	3-G[a] Gasoline	3-G[a] Diesel oil	3-G[a] White oil	4-G[a] Gasoline	4-G[a] Diesel oil	4-G[a] White oil
PHILIPS MiniPal EDXRF spectrometer	1	20.7	29.9	45.1	10.7	36	45.7	5.8	20.5	29.9	47.4	48	56.9
	2	20.4	29	39.8	9.8	36.1	46.3	6.4	20.6	29.8	40.1	48.1	64.1
	3	20.2	28.7	45.7	13.6	39	49.9	4.1	23.2	26.4	46.9	46.7	63.2
	4	16.3	28.4	36.9	10.1	33.3	43.7	4.1	23.3	29.1	46.8	44.2	66.7
	5	16.8	30.8	38.9	12.8	37.1	45.9	5.2	18.9	25.7	47.1	41.1	69.8
	Mean (ppm)	18.9	29.4	41.3	11.4	36.3	46.3	5.1	21.3	28.2	45.7	45.6	64.1
	S.D. (ppm)	2.1	1.0	3.9	1.7	2.1	2.2	1.0	1.9	2.0	3.1	3.0	4.8
	R.S.D. (%)	11.3	3.3	9.5	14.9	5.7	4.9	20.0	8.9	7.0	6.8	6.5	7.5
	LLD (ppm)	0.8	0.8	0.8	0.8	0.8	0.9	0.8	0.8	0.8	0.9	0.9	0.9
	C (ppm)	6.3	2.9	11.6	5.0	6.1	6.7	3.0	5.6	5.9	9.2	8.8	14.2
APS 35^{TM} Elemental Analyser	1	12.7	15.0	10.9	21.9	23.9	20.1	6.9	9.4	5.1	9.2	11.6	7.4
	2	12.6	15.0	10.9	22.5	24.5	20.7	6.4	8.9	4.6	9.1	11.5	7.3
	3	13.3	15.6	11.6	22.4	24.4	20.6	6.7	9.2	4.9	8.7	11.2	7.0
	4	13.0	15.3	11.2	22.7	24.7	21.0	6.8	9.2	5.0	8.9	11.3	7.1
	5	13.6	15.9	11.8	23.0	25.0	21.2	6.4	8.9	4.6	9.2	11.6	7.4
	Mean (ppm)	13.0	15.3	11.3	22.5	24.5	20.7	6.6	9.1	4.9	9.0	11.4	7.2
	S.D. (ppm)	0.4	0.4	0.4	0.4	0.4	0.4	0.2	0.2	0.2	0.2	0.2	0.2
	R.S.D. (%)	3.1	2.6	3.6	1.8	1.6	2.0	3.4	2.3	4.7	2.2	1.7	2.7
	LLD (ppm)	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.8	0.8	0.8	0.8	0.8
	C (ppm)	±1.2	±1.2	±1.2	±1.2	±1.2	±1.2	±0.7	±0.6	±0.7	±0.6	±0.6	±0.6
Instrument	Matrix	1-D Gasoline	1-D Diesel oil	1-D White oil	2-D Gasoline	2-D Diesel oil	2-D White oil	3-D Gasoline	3-D Diesel oil	3-D White oil	4-D Gasoline	4-D Diesel oil	4-D White oil
PHILIPS MiniPal EDXRF spectrometer	1	12.7	30.2	39.8	3.9	17.7	25.4	3.5	9.3	15.6	15.4	17.7	22.3
	2	9.2	26.6	45.1	4.3	19.8	29.7	3.7	11.5	19.2	9.8	26.3	20.1
	3	9.9	28.9	43.9	3.5	15.3	24.1	5.9	11.6	16.3	12.9	16.8	21.4
	4	10	31.1	45.4	4.7	19.5	25.8	4.2	9.4	18.7	11.9	19.7	23.1
	5	13.4	29.4	42.1	6.1	16.2	23	3.4	9.4	16.9	13.9	18.4	23.4
	Mean (ppm)	11.0	29.2	43.3	4.5	17.7	25.6	4.1	10.5	17.3	12.8	19.8	22.1
	S.D. (ppm)	1.9	1.7	2.3	1.0	2.0	2.5	1.0	1.3	1.6	2.1	3.8	1.3
	R.S.D. (%)	17.0	5.8	5.4	22.2	11.2	9.9	24.9	12.2	8.9	16.5	19.2	6.1
	LLD (ppm)	0.8	0.8	0.8	0.9	0.8	0.8	0.9	0.8	0.9	0.8	0.8	0.8
	C (ppm)	5.6	5.0	6.9	3.0	5.9	7.5	3.1	3.8	4.6	6.2	11.2	4.0
APS 35^{TM} Elemental Analyser	1	22.5	24.6	20.8	32.9	34.6	31.2	8.1	10.6	6.4	20.1	22.2	18.4
	2	22.7	24.7	20.9	33.1	34.8	31.4	7.8	10.3	6.0	20.3	22.4	18.5
	3	23.1	25.1	21.3	33.8	35.4	32.0	7.6	10.3	5.8	21.4	23.4	19.6
	4	22.6	24.6	20.8	33.9	35.6	32.1	7.8	10.4	6.0	22.3	24.3	20.6
	5	22.7	24.7	20.9	33.1	34.8	31.4	7.9	10.5	6.2	23.3	25.3	21.6
	Mean (ppm)	22.7	24.7	20.9	33.4	35.0	31.6	7.8	10.4	6.1	21.5	23.5	19.7
	S.D. (ppm)	0.2	0.2	0.2	0.4	0.4	0.4	0.2	0.1	0.2	1.4	1.3	1.4
	R.S.D. (%)	1.0	0.9	1.1	1.3	1.2	1.4	2.6	1.4	3.6	6.3	5.6	6.9
	LLD (ppm)	0.8	0.8	0.8	0.8	0.8	0.8	0.7	0.8	0.8	0.7	0.8	0.8
	C (ppm)	±0.7	±0.6	±0.7	±1.3	±1.3	±1.3	±0.6	±0.4	±0.6	±4.0	±3.9	±4.0

[a] Using different hydrocarbon matrices.

calculated peak intensity calculated from the profile (using same width). The confidence interval was calculated with Eq. (6).

$$C = m \pm \frac{t\text{S.D.}}{\sqrt{n}} \qquad (6)$$

In this equation the m, n and S.D. represents the mean, number and standard deviation of measurements, t is the Student variable function (with acceptance reliability level of 99.7%).

The sulphur concentration in liquids measured with different analytical methods using hydrocarbon matrices with different ratio of C/H was compared in Figs. 7–9 indicated. A considerable effect of the hydrocarbon matrix was found. Not only the standards used with different ratio of C/H affected the accuracy of different analytical methods, but also

Table 6
Results of experiments of commercial fuels

	Method					
	APS 35^{TM}			PHILIPS MiniPal EDXRF spectrometer		
	Gasoline 1[a]	Gasoline 2[a]	Diesel[a]	Gasoline 1	Gasoline 2	Diesel
Experimental results						
1	5.4	42	260.8	5.3	38.7	254.8
2	4.9	42	256.4	4.4	39.3	258.7
3	5.1	46	261.3	4.7	38.1	260.0
4	4.6	42.7	260.4	5.1	37.0	256.0
5	4.9	43.3	254.9	5.0	38.1	259.0
6	5.2	44	256.0	5.4	35.8	258.8
7	4.7	42.1	261.5	5.0	39.4	261.8
8	4.8	39.4	269.4	7.0	37.4	261.1
9	4.8	45.1	261.8	6.2	37.1	260.0
10	4.8	44.6	237.5	7.3	40.9	261.0
11	4.0	45.2	263.0	7.9	42.8	257.9
12	4.8	44.3	257.3	7.3	41.0	260.1
13	5.2	43.3	262.5	7.9	39.4	259.9
14	4.9	39.6	264.8	6.8	40.2	261.8
15	5.3	42.6	249.7	7.8	43.1	261.0
16	5.2	44.7	255.9	8.0	41.9	260.9
17	5.2	43.6	258.8	7.8	44.0	258.7
18	5.0	43.6	268.9	8.1	43.6	262.4
19	5.0	43.6	269.4	8.4	42.0	257.1
20	5.3	45.4	260.2	8.5	44.6	260.7
1–20						
Mean (ppm)	5.0	43.4	259.5	6.7	40.2	259.6
S.D.	0.3	1.8	7.2	1.4	2.6	2.0
R.S.D. (%)	6.3	4.0	2.8	21.0	6.5	0.8
LLD	0.8	0.9	1.5	1.0	1.0	1.4
C (ppm)	±0.4	±2.6	±10.6	±0.5	±3.8	±2.9
1–10						
Mean (ppm)	4.9	43.1	258.0	5.5	38.2	259.1
S.D.	0.2	1.9	8.3	1.0	1.5	2.2
R.S.D. (%)	4.1	4.3	3.1	17.5	3.8	0.8
LLD	0.8	0.9	1.5	1.0	1.0	1.4
C (ppm)	±0.4	±3.9	±17.3	±2.1	±3.1	±4.6
11–20						
Mean (ppm)	5.0	43.6	261.1	7.9	42.3	260.1
S.D.	0.4	1.7	6.0	0.5	1.7	1.7
R.S.D. (%)	8.0	3.9	2.3	6.3	4.0	0.6
LLD	0.8	0.8	1.5	1.0	1.0	1.4
C (ppm)	±0.8	±3.6	±12.5	±1.0	±3.6	±3.6

[a] Sample.

the composition of matrices (e.g. aromatic content). Samples from 1-G to 3-G gave good correlation between the results measured in gasoline matrix by methods. This matrix had the lowest value of C/H. This behaviour may be attributed to a lower value of C/H in case of samples with "G" symbols (from 1-G to 4-G). As it was shown in Table 1 samples "G" consisted of the lighter fractions and the "D" symbol refers to heavier fraction with higher C/H ratio. With increasing ratio of C/H of the standard matrices the difference between the results of the two methods significantly increased. It was earlier described that the ratio of C/H might have a considerable effect on accuracy [14]. It can be explained with the emission of X-ray photons from carbon atoms, which could increase the background scattering. In the APS 35^{TM} elemental analyser the samples were combusted into different oxides, but the detector senses only the sulphur-dioxide, therefore the C/H ratio has no significant effect on the accuracy and the value of measured concentration. This phenomenon was the cause of that no significant differences observed in the calibration graphs and the results of measurements in case of APS 35^{TM} elemental analyser. According to data shown in Table 4, the results of experiments using APS 35^{TM} elemental analyser had no divergence in case of different matrices, whereas increasing tendency in means of experimental results were observed in case of EDXRFS method.

In case of Sample 4-G the deviation of means was significantly greater by the use of all calibration graphs at EDXRFS method. This can be attributed to its aromatic

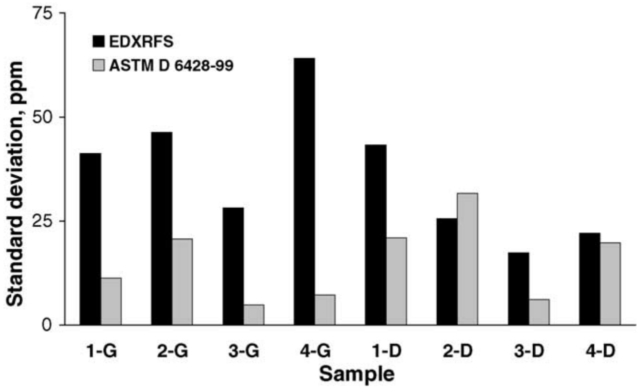

Fig. 9. The average of the concentration of sulphur using standards in white oil matrix and different instruments.

content. Sample 4-G was obtained by the thermal cracking of polystyrene containing waste polymer blend and consequently, it had an aromatic content of 25.9%, which significantly deteriorated results.

Samples from 1-D to 4-D contain heavier hydrocarbon molecules with higher value of C/H ratio. As Figs. 7–9 indicate that the results become less different with calibration graphs in diesel oil and white oil matrices than in matrix of gasoline.

3.2. Investigation of sulphur content in commercial fuels

In this part of our experiments, commercial fuels (gasoline and diesel oil) were measured according to ASTM D6428-99 and with PHILIPS MiniPal PW 4025/02 EDXRF spectrometer. Both samples were obtained from a filling station of MOL PLC. Gasoline was measured with gasoline calibration graph and diesel fuel with a diesel fuel calibration in case of both instruments. All samples were measured immediately, twenty times successively. Results are summarized in Table 6.

As Table 6 indicates no significant differences were observed between the two methods. The measurements of gasoline samples resulted in differences in sulphur content of 1.8 ppm and 3.1 ppm in case of Gasoline 1 and Gasoline 2, respectively and 0.1 ppm in case of diesel oil. A considerable difference was found between the means of measurements 1–10 and 11–20, but it was significant only in case of the EDXRFS method. It was found that the means of measurements 1–10 were smaller than in case of measurements 11–20 with respect to all samples and both instruments. This behaviour could be attributed to the partial evaporation of samples resulting in high sulphur concentrations.

4. Conclusion

There are very few standards to determine the concentration of sulphur in the products of the petroleum industry. Two analytical methods for the determination of sulphur concentration were compared. The concentration of sulphur was measured in various hydrocarbon matrices of different ratio of C/H. In case of EDXRFS significant matrix effect could be observed, and the properties of calibration graphs significantly deviated from each other. A similar phenomenon was not found when using sample combustion methods. Liquids obtained by thermal degradation of waste plastics were analysed with both methods. Good similarity was found between different analytical methods, but the matrices of standard samples had a considerable effect on the accuracy. The matrix effect was more significant with the EDXRFS method and less considerable using APS 35$^{\text{TM}}$ elemental analyser. Results were affected not only by the ratio of C/H of samples, but also by their hydrocarbon structure (e.g. aromatic content). The greater discrepancy between the two methods was observed in case of Sample 4-G, which had significant aromatic content. In the case of commercial fuels, it was thought that the considerable error in the average and standard deviation in case of gasoline samples might be caused by the evaporation of samples. To summarize, both of the compared analytical techniques gave good accuracy. In case of adequate calibration graphs for EDXRFS the disturbing effect of the C/H ratio could be eliminated.

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 PLC for financial support received for this work. Special thanks to the A Testor Ltd.

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