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A New Method for the Determination of S, V, Fe, Ni, Pb and Other Elements in Some Distilled Fractions of Crude Petroleum by TXRF

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ABSTRACT: The possibility of employing the Total Reflection X-ray fluorescence (TXRF) technique for the analysis of some derivatives of petroleum crude oil (Petrol, Diesel oil, Fuel oil), is demonstrated with the help of certified standards (NIST, ENEL, ICIP). The quantitative analysis is conducted via an internal standard method. Some problems about elements volatility (S in Diesel oil and Pb in Petrol) are solved to permit an accurate quantitative simultaneous determination of the elements (from $Z = 13$ to $Z = 90$ with a detection limit in the range from ppb to ppm) present in the samples of petroleum derivatives. The analyses are conducted with a new Total Reflection X-ray spectrometer (TX 2000 supplied by Ital Structures)

1. INTRODUCTION

The most important metallic and non-metallic elements found in the distilled fractions of crude petroleum are S, Ca, V, Mn, Fe, Co, Ni, Pb with concentrations varying from parts % to ppm. Some of these elements are found in the form of organic and inorganic salts, organometallic compounds or chelates. The sulphur is contained in some organic compounds: thioalcohols, thioethers, thiophenols, thiophene, sulphidric acid and elemental sulphur. The lead contained in the petrol is added in the form of the antidetonant compounds tetraethyl lead and tetramethyl lead.

There are many reasons for interest in the quantification of these elements. The sulphur always contained in the distilled fractions is a source of environmental pollution. The same is also true for the lead in petrol. The presence or absence of other elements can be used to distinguish between different types of oil or to show its migration and accumulation in deposits (1 and 2). Of great interest is the ability to monitor the presence of these elements with a detection limit applicable in the context of environmental health. We aim to demonstrate that the quantitative analysis of these elements in crude oil samples can be satisfactorily conducted using an internal standard method.

2. TXRF PRINCIPLES

In principle, analysis of X-ray fluorescence in total reflection (3, 4, 5) is the same as conventional X-ray fluorescence measurement using energy analysis, but it uses a special geometrical arrangement to maximise the ratio between useful signal and background noise. When radiation passes from a medium of lower density to one of a

higher density it is totally reflected provided the angle of incidence is below a certain critical angle, typically a few milliradians for X-rays. Beam penetration into the reflecting surface is minimal. By illuminating the sample in a beam that is being totally reflected, absorption of the beam in the supporting substrate is largely avoided thereby and with it the associated scattering and background noise.

A further contribution to the reduction of background noise is obtained by minimising the thickness of the sample. A small drop of the sample (10-100 μl of the substance dissolved in an appropriate solvent) is placed on a optically flat fused silica carrier. On evaporation of the solvent a thin film a few nanometers thick remains. In use the greater part of the scattering which normally arises from the sample and its matrix is eliminated.

Fig.1 TX 2000 geometry.

3.EXPERIMENTAL

3.1 Treatment of the samples

One of the most important feature of TXRF is the ability to achieve an accurate quantitative analysis using a single internal standard. We use a water standard solution, which is cheap and readily available and to permit the mixture with the oil sample we use THF solvent.

Sample materials and standardised petroleum oils (Tab 1), supplied by Messrs Italiana Energia e Servizi S.p.A IES, oil refinery of Mantova, have been treated as follows:

Petrol: we had to quantify the lead concentration. The problem was the high volatility of the lead compounds (tetraethyl and tetramethyl lead). We solved this by mineralising the lead. We prepared a solution using THF (500 μl Carlo Erba RPE), HNO_3 65% (100 μl Merck Suprapur) with Ga 1000 ppm (10 μl Merck standard solution) as internal standard. We added 100 μl of petrol sample to it, so that the nitric acid present in the solution made the lead into the non-volatile $\text{Pb}(\text{NO}_3)_2$. Now we pipetted 10 μl of this solution on the sample holder and evaporated it by IR light.

Diesel oil: we had to quantify the sulphur concentration, the problem was now the high volatility of the sulphur compounds when the sample is evaporated. We prepared a solution with THF (1 ml Carlo Erba RPE), sample (100 μl Diesel oil) and Ga 1000 ppm (10 μl Merck standard solution) as internal standard. Then we pipetted only 5 μl onto the sample holder and measured the sample without evaporating it. In

this mode the background scattering is not high and a very accurate sulphur quantification is possible.

Fuel oil: we had to quantify some elements, the problem was the high viscosity and the consequent lack of homogeneity in the sample as supplied. We have referred to the method illustrated in Ref. 3 to homogenise the sample. We prepared a solution with THF (about 2 ml Carlo Erba RPE), sample (about 0.1 g Fuel oil) and Ga 1000 ppm (100 µl Merck standard solution) as internal standard and we pipetted 10 µl of this solution onto the sample holder and evaporated it by heating.

The quantity of sample, standard and solvent in the solution could differ but they are always exactly weighed (± 0.1 mg).

3.2 Measurements

Before depositing the sample we controlled the cleanliness of the sample holder by making a measurement with it empty. In the same way we checked the solvents used. Then we deposited the samples as described in the sample treatment. For each sample we repeated the measurement at least 5 times. The voltage and the current used in the measurements were always 35 kV and 30 mA, and the measuring times varied from 200 s to 500 s.

The spectra were analysed by the quantitative analysis software WinTXRF supplied by Ital Structures and checked with the QXAS-AXIL package supplied by the IAEA of Vienna.

The results are given in Tab 1 and Tab 2.

STANDARD SAMPLE	CERTIFIED ELEMENTS QUANTITY	TXRF MEASURED (N=5) ELEMENTS QUANTITY	% DIFFERENCE
O.C. NIST 1619 a	S (0.725 $\pm$ 0.007) % wT	S (0.755 $\pm$ 0.007) % wT	4
DIESEL OIL STANDARD ICIP	S 1.60 % wT	S (1.48 $\pm$ 0.2) % wT	7
HEAVY DIESEL OIL STANDARD ICIP	S 2.45 % wT	S (2.45 $\pm$ 0.3) % wT	0
O.C. ENEL	Ni (53.1 $\pm$ 1.1) ppm V (410.1 $\pm$ 10.5) ppm	Ni (54 $\pm$ 4) ppm V (410 $\pm$ 30) ppm	1.7 0.02
PETROL STANDARD ICIP	Pb 0.323 g/l	Pb (0.324 $\pm$ 0.016) g/l	0.3
O.C. NIST 1634 b	S (2.80 $\pm$ 0.05) % wT Fe (31.6 $\pm$ 2.0) ppm Mn (0.23 $\pm$ 0.03) ppm Ni (28 $\pm$ 2) ppm Sc (0.18 $\pm$ 0.04) ppm V (55.4 $\pm$ 1.1) ppm	S (2.94 $\pm$ 0.3) % wT Fe (28 $\pm$ 3) ppm Mn < 1 ppm Ni (29 $\pm$ 3) ppm Sc < 1 ppm V (60 $\pm$ 4) ppm	5 11 3 8
DIESEL OIL BTZ STANDARD ICIP	S 0.048 % wT	S (0.048 $\pm$ 0.007) % wT	0
O.C. ENEL	Ni (22 $\pm$ 1.5) ppm V (15.8 $\pm$ 1.2) ppm	Ni (25 $\pm$ 2) ppm V (15 $\pm$ 2) ppm	12 5
DIESEL OIL STANDARD ICIP	S 0.098 % wT	S (0.092 $\pm$ 0.005) % wT	6
PETROL STANDARD ICIP	Pb 0.172 g/l	Pb (0.168 $\pm$ 0.008) g/l	2

Tab.1

SAMPLE	TXRF MEASURED (N=5) ELEMENTS QUANTITY
COMMERCIAL PETROL	Pb (0.146 ± 0.01) g/l
DIESEL OIL CORR. UNICHIM 1/95	S (480 ± 30) ppm
DIESEL OIL S.38	S (620 ± 46) ppm
DIESEL OIL S.33	S (408 ± 28) ppm

Tab. 2

Some characteristic spectra are shown here. Note the very low background for the samples. This feature permits us to reach detection limits of 9 ppb for Pb in Petrol, about 50 ppm for S in Diesel oil and about 0.1 ppm for the metals in Fuel oil.

LEGEND: The peaks are due to the K and L transitions. Si, Ar and Au signals are due to glass sample holder, air and the detector respectively.

Petrol Standard ICIP Pb 0.324 g/l. Mo source 35 kV, 30 mA. 10 μ l, live time 200s

Diesel Oil Standard ICIP S 1.6%. Mo source 35 kV, 30 mA. 5 μ l, live time 300s.

Fuel Oil Standard O.C. NIST 1634 b. Mo source 35 kV, 30 mA. 10 μ l, live time 300s.

Fuel Oil Standard O.C. ENEL V 410 ppm Mo source 35 kV, 30 mA. 10 μ l, live time 300 s.

3.3 Data analysis

WinTXRF is software for the quantitative analysis of energy dispersive Total Reflection X-ray fluorescence. The fitting algorithm is an iterative chi-square Marquart routine based on a sum of Gaussian peaks. Then the concentration of analyte is calculated as follows:

$$C_x = C_{is} * RF * I_x / I_{is}$$

where: C_x is the unknown analyte concentration
 C_i is the internal standard concentration
 I_i is the area of the peak due to the internal standard
 I_x is the area of the peak due to the analyte
 RF is the fluorescent yield

RF is a curve found by experiment.

We report on only the mentioned elements but we have quantified all the other elements present at the same time. We used the same RF curve for the quantification of all the elements present in Petrol and Fuel oil. For Diesel oil we used a different curve because the sample in this case was not evaporated.

3.4 Apparatus

We used the TX 2000 X-ray spectrometer manufactured by Ital Structures. The geometry for X-ray fluorescence in total reflection is shown in Fig. 1. A primary beam provided by the X-ray tube with a molybdenum or other appropriate metal-anode is monochromatised and is made to fall on the sample at an angle less than the critical angle.

The fluorescent energy derived from the sample is detected in the solid state lithium-drifted silicon detector which is cooled with liquid nitrogen.

The signal from the detector is processed in a counting chain (preamplifier, amplifier, analogue to digital converter) attached to a personal computer via an interface card which emulates a multichannel analyser and display controller. Of special note is the fact that the use of this solid state detector allows a resolution of 137 eV for Mn $K\alpha$.

The monochromator and the characteristics of the detector (high resolution and thin beryllium window) further improve the high detection limit typical of the TXRF method. The TX 2000 detection limit is shown in Fig. 2.

Fig.2 Detection limit vs. atomic number of TX 2000 Spectrometer, Mo source 35 kV, 30 mA

4. CONCLUSIONS

We have verified the powerful method of the TXRF analysis for metallic and non-metallic elements determination for some distilled petroleum fractions.

An accurate quantitative simultaneous determination of the elements (from $Z=13$ to $Z=90$ with a detection limit in the range from ppb to ppm) is possible due to the absence (which is an inherent feature of TXRF) of matrix effects. Some problems due to the volatility of the elements (S in Diesel oil and Pb in petrol) have been solved.

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