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A Fast Method to Determine Sulphur Content in Petroleum Products - X-Ray Fluorescence

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Abstract

This work presents a very reliable tool for the analysis laboratories in the petrochemical field – Energy Dispersive X-ray Fluorescence (EDXRF) and results obtained by our team. Knowing the concentration in which the sulphur is present in petroleum products is of great importance, due to the components that can appear after burning the products (as sulphur oxides), components that can affect in great measure the environment. The use of EDXRF makes the analysis faster, more reliable and less hazardous for the analyst.

Key words: *sulphur, petroleum products, EDXRF*

Introduction

Our society deals in these days with a serious problem, environment pollution. This is the result of industrial development, the emission of various toxic gases (sulphur oxides, nitrogen oxides, volatile organic compounds and others), powders and aerosols having a destructive action on the environment.

All the producers involved in the petroleum industry tries to reduce the content of sulphur in their fuels, due to the effect that sulphur compounds have on people, but also on stone and metal constructions.

Our work intends to present the results obtained by a very modern analytical technique, Energy Dispersive X-Ray Fluorescence (EDXRF), easy to apply when working with petroleum products. In past papers, we have presented it's applications in various other domains [1, 2].

Experimental

Fundamentals of EDXRF

X-ray fluorescence (XRF) spectrometry is an elemental analysis technique with broad application in science and industry. XRF is based on the principle that individual atoms, when excited by an external energy source, emit X-ray photons of a characteristic energy or wavelength. By counting the number of photons each energy emitted from a sample, the elements present may be identified and quantified.

The identification of elements by X-ray methods is possible due to the characteristic radiation emitted from the inner electronic shells of the atoms under certain conditions. The emitted quanta of radiation are X-ray photons whose specific energies permit the identification of their source atoms.

When an electron beam of high energy strikes a material, one of the results of the interaction is the emission of photons which have a broad continuum energy. This radiation, called *bremsstrahlung*, or "braking radiation" is the result of the deceleration of the electrons inside the material. Another result of the interaction between the electron beam and the material is the ejection of photoelectrons from the inner shells of the atoms making up the material. These photoelectrons leave with a kinetic energy (E-φ) which is the difference between that of the incident particle (E) and the binding energy (φ) of the atomic electron. This ejected electron leaves a "hole" in the electronic structure of the atom, and after a brief period, the atomic electrons rearrange, with an electron from a higher energy shell filling the vacancy. By way of this relaxation the atom undergoes *fluorescence* or the emission of an X-ray photon whose energy is equal to the differences in energies of the initial and final states (figure 1) [3]. Detecting this photon and measuring its energy allows us to determine the element and specific electron transition from which it originated [4]. Herein lies the basis of XRF spectrometry, where elements may be quantitated based on the rate of emission of their characteristic X-rays from a sample that is being excited.

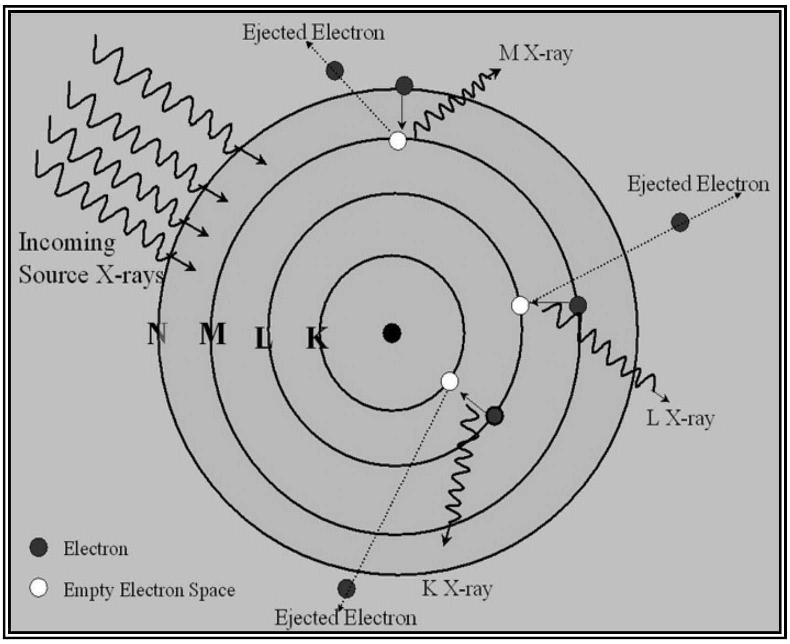

Fig. 1. XRF process inside the atom

Any of the electrons in the inner shells of an atom can be ejected, and there are various electrons in the outer shells that can "drop" to fill the void. Thus there are multiple types of allowed transitions that occur which are governed by the laws of quantum mechanics. The three main types of transitions or spectral series are labelled K, L or M corresponding to the shell from which the electrons was initially removed. Within the series, the specific transitions are denoted by the subscripts α, β, γ, etc. to denote which upper energy shell was involved in the relaxation, and finally a numerical subscript to indicate the quantum state within that upper energy shell.

Most of the XRF instruments (figure 2) in use today fall into two categories: energy dispersive (ED) and wavelength dispersive (WD) spectrometers, the main difference between them being the way they make the quantification: from the energy or from the wavelength.

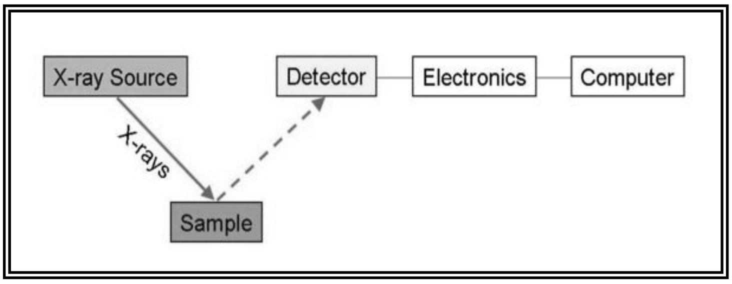

Fig. 2. Schematic representation of XRF instruments

Apparatus

The spectrometer used for the determination was a PW 4025 MiniPal Energy-Dispersive X-ray Spectrometer with Rh anode (fig. 3). The elements that can be measured are from Na (*Z*=11) to U (*Z*=92), due to the very small fluorescence of the elements with *Z* smaller than 11. The spectrometer can be operated up to 30 kV.

All the calculations are made automatically, by the dedicated software.

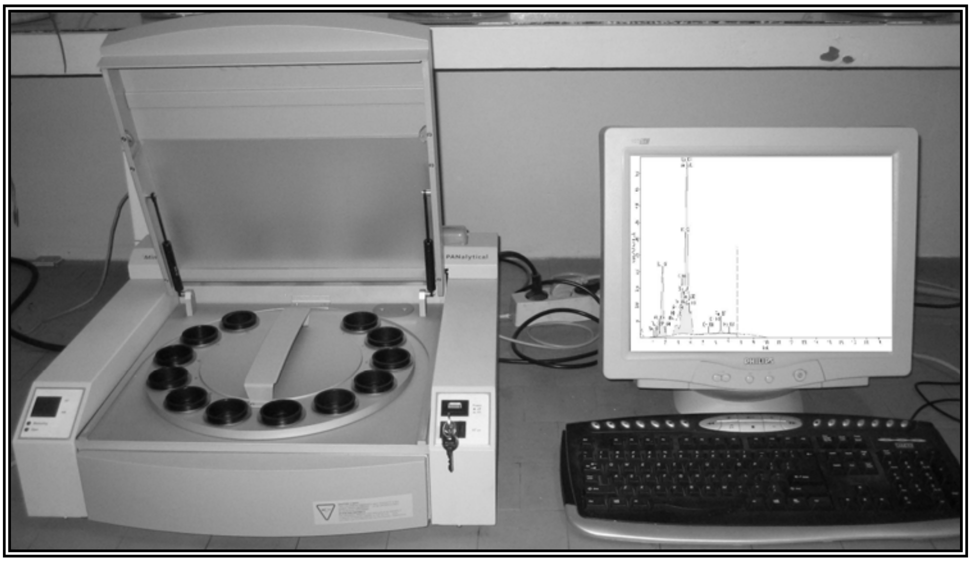

Fig. 3 The EDXRF spectrometer MiniPal PW 4025

To prepare the standards, we used sulphur certified reference material (5%) and base oil, commercially available.

Results and Discussion

First of all, the parameters must be chosen carefully, in order to excite sulphur in the petroleum products, and to have the best response from the sample.

To reach the appropriate parameters, measurements was carried under different conditions:

- all other parameters were kept constant, and the tension varied (5, 10, 15, 20, 25, 30 keV);
- all other parameters were kept constant, and the intensity varied (2, 50, 100, 200, 300 μA);

- o all other parameters were kept constant, and the filter was changed (Al, Al-thin, kapton, no filter);
- o all other parameters were kept constant, and the working atmosphere changed (air or helium);
- o all other parameters were kept constant, and the measuring time varied (20, 50, 100, 150, 200, 250, 300 seconds).

For the repeatability, then measurements were conducted under the experimental established parameters, as described above (5 keV, 300 mA, no filter, helium atmosphere, 300 seconds).

In figure 4 it is shown the EDXRF specific spectrum for sulphur, obtained experimentally.

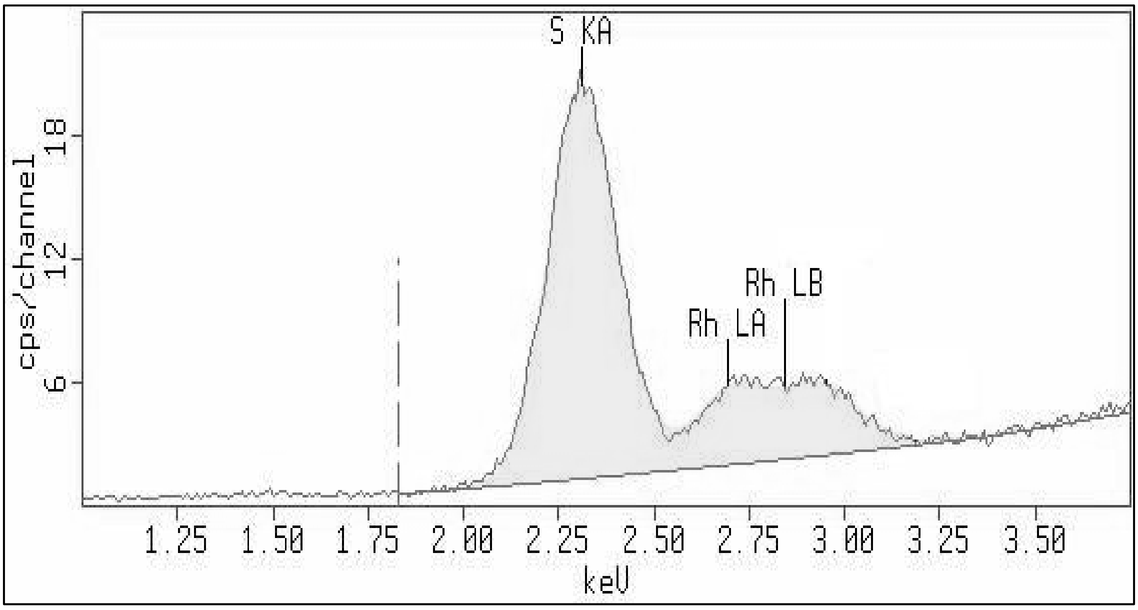

Fig. 4. Characteristic EDXRF spectrum for sulfur

The calibration curve obtained has a very good correlation factor (0.999945), for the domain 0-5% (figure 5).

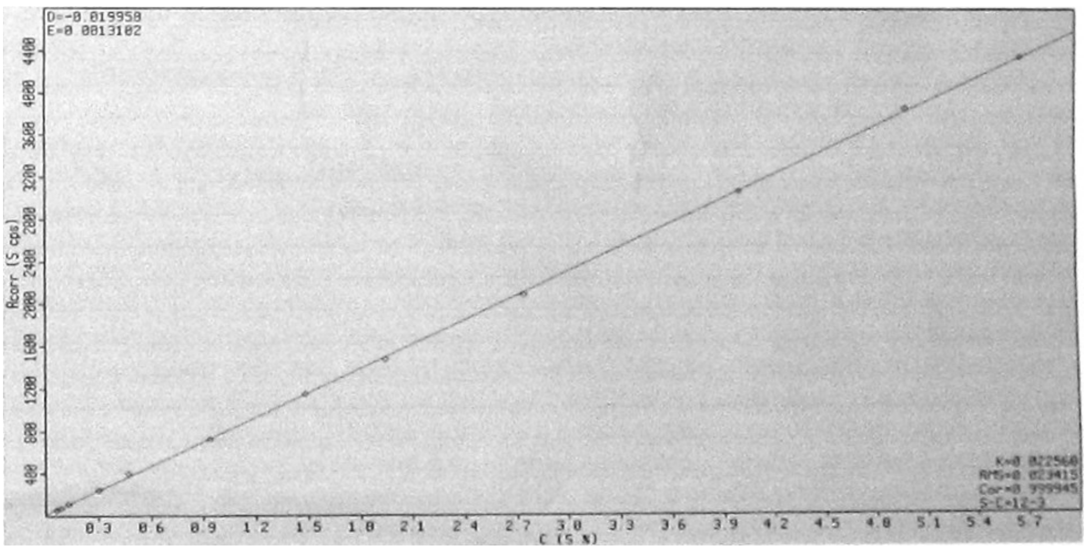

Fig. 5. Correlation curve for sulphur concentration 0-5%

The results for repeatability are presented in table 1, also showing a very small standard deviation.

Table 1. Repeatability results, for 10 concentrations, each mean concentration being the result of ten measurements

Sample	Mean concentration (%)	Standard deviation (%)
1	0.3	0.001
2	0.7	0.0011
3	1	0.009
4	1.5	0.001
5	2.0	0.0012
6	2.5	0.0011
7	3.0	0.0095
8	3.5	0.0012
9	4.0	0.001
10	4.5	0.0011

Conclusions

In our days, when the environment pollution reached a level that affects all living creatures, the control of potentially harmful compounds is essential. Among very hazardous compounds are the compounds with sulphur, many obtained from burning sulphur-containing petroleum products.

In our work, we have presented a very fast and reliable method, which can be applied to all petroleum products as we have demonstrated.

Even if working with radiation is often considered hazardous, and the base radioprotection principle states that radiation-involved techniques must be used only when other methods are not applicable, the method described above involves small or none contamination risks, under normal operation. Also, it can replace methods far more dangerous to the operator.

References

1. Fierascu, R.C., Dumitriu, I., Munteanu, V. – Monitoring of soils charged with heavy metals. *Analele Universitatii din Bucuresti – CHIMIE*, 2007, pp 87-92.
2. Ion, R.M., Ion, M.L., Niculescu, V.I.R., Dumitriu, I., Fierascu, R.C., Florea, G., Bercu, C., Serban, S. – Spectral analysis of original and restored ancient paper from Romanian gospel. *Romanian Journal of Physics*, Vol. 53, nr. 5-6, 2008.
3. Bertin, E. P. – *Principles and Practice of X-ray Spectrometric Analysis.* Kluwer Academic / Plenum Publishers.
4. Jenkins, R. – *X-ray Fluorescence Spectrometry.* John Wiley & Sons, Inc., 1988.

O metodă rapidă pentru determinarea sulfului din produse petroliere – Fluorescența de raze X

Rezumat

Această lucrare prezintă un instrument foarte eficient pentru laboratoarele de analize din domeniul petrochimic – Fluorescența de raze X cu dispersie după energie (EDXRF) şi rezultatele obținute de colectivul nostru. Cunoaşterea concentrației în care sulful este prezent în produsele petroliere este foarte importantă, din cauza compuşilor care pot apărea după arderea produselor (cum ar fi oxizii de sulf), compuşi care afectează în mare măsură mediul înconjurator. Folosirea EDXRF face ca analiza să fie mai rapidă, mai eficientă şi mai putin periculoasă pentru analist.