

# Petrochemical Applications of an Entry Level Wavelength Dispersive XRF Spectrometer (WDXRF)

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**Abstract :** X-Ray Fluorescence (XRF) is a well established technique in the petrochemical industry. The availability of cost-effective entry level WDXRF, requiring no external water or detector gas has facilitated the widespread use of this technique. This paper describes the performance of a low power WDXRF instrument for the analysis of sulfur in petrochemical products. It reviews various methods that have been applied and their performance in terms of repeatability.

## 1. INTRODUCTION

Whereas wavelength dispersive spectrometers (WDXRF) using high power (above 2kW) are mainly used in central laboratories for a wide range of applications (oils, polymers, catalysts, geological materials and other organic matrices), the analysis of elements such as S, Ni, V, Pb and certain elements of process control in refineries, can be carried out by energy dispersive (EDXRF) or wavelength dispersive (WDXRF) techniques equipped with X-ray tubes with lower power.

The use of WDXRF instruments for the dosage of elements such as Si, S, Pb, Ni, V, Cl, Br is particularly suited to the requirements of certain standard methods and the increasing need to analyze lower and lower contents. Different analytical methods are being used in the industry, including use of gross peak intensities, nett peak intensities, internal standards and are constantly being improved for better precision, reliability and easier use. This is allowing the operators in the various pilot units to monitor elemental content by carrying out the analysis themselves.

The Institut Français du Pétrole (IFP) has acquired an ARL OPTIM'X WDXRF from Thermo Electron Corporation for its laboratory based in Lyon, France (Figure 1). Equipped with a low power tube (50W), the instrument is being used for the self-service monitoring of sulfur in the various oils and fuel samples obtained through different processes currently under investigation at the IFP. The main advantages of this solution include the processing speed of the analysis with the constant availability of the apparatus and the ease of use of the instrument as a self-service tool, while at the same time offering performances comparable to those of a high power system.

Figure 1: The Institut Français du Pétrole (IFP) site in Lyon



## 2. INSTRUMENT CONFIGURATION

The spectrometer (Figure 2) can be used with a goniometer and/or fixed channels allowing highly flexible configurations to suit the needs of the users' laboratories. The IFP has chosen to install two fixed channels for the measurement of  $SK_{\alpha}$  and  $S_{background}$  intensities.

Figure 2 (left): The ARL OPTIM'X WDXRF spectrometer from Thermo Electron Corporation is installed at the IFP- Lyon.

## 3. DETERMINATION OF THE MINIMUM VOLUME

The various processes studied on pilot plants (Figure 3) at the IFP imply availability of only very small volumes of samples. Although the WDXRF technique is non destructive for the sample, sample taking has been reduced to a



Figure 3: Pilot units in the new hall at IFP- Lyon.

minimum without any noticeable deterioration in the quality of the analytical results.

The variations in the measured signal relating to the sample volume enabled an assessment of the minimum volume of sample required for which the measured signal no longer varied. These practical trials were verified by calculating the theoretical volume necessary to work in infinite thickness.

### 3.1 Experimental determination of the minimum volume

The following graphs indicate the variation in the  $SK_{\alpha}$  signal expressed in kilocounts per second, considering the volume of the sample used, for two different concentrations of 38ppm and 0.72%.

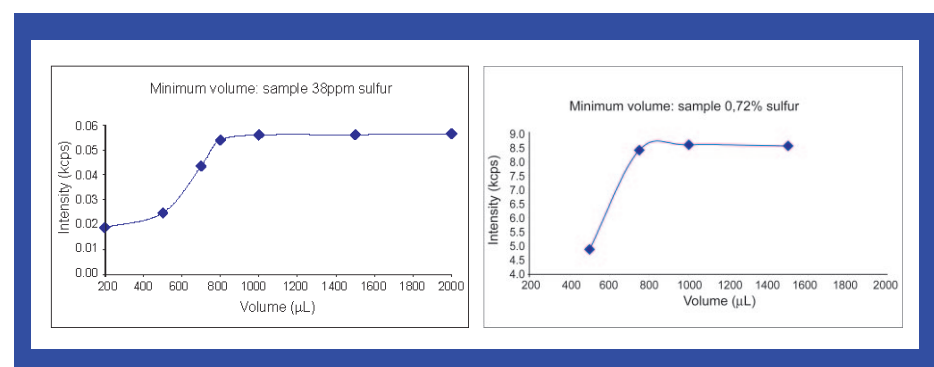


Figure 4 : Relation between sample volume and sulfur intensity – low level sulfur

Figure 5 : Relation between sample volume and sulfur intensity – high level sulfur

These two different types of concentrations show a constant signal starting with a sample size of about 0.8ml. For safety reasons, the sample size was set at 2ml. It is clear that this test has allowed a considerable reduction of the sample size, since the volume usually required by the laboratory to carry out the same measurement was 30 ml up to now.

### 3.2 Theoretical determination of the minimum volume

In the monochromatic approximation ie. excitation of the  $SK_{\alpha}$  transition by the  $RhL_{\alpha}$  radiation of the X-ray tube- the intensity or fluorescence,  $I_e$ , depends on the thickness of the sample (expressed as  $e$ ), on the sample density  $\rho$  and its average mass absorption coefficient  $\mu_m$ .

From a thickness, labeled  $e_{\infty}$ , the fluorescence signal,  $I_{\infty}$ , becomes constant. This gives the following standard equation:



$$I_e = I_\infty (1 - \exp(-\rho \mu_m e))$$

with  $\mu_m = \mu(\text{RhL}_\alpha)/\sin(\theta_1) + \mu(\text{SK}_\alpha)/\sin(\theta_2)$ ,  $\theta_1$  and  $\theta_2$  being the excitation and emission beams angles.

The variations of  $I_e$  are regarded as constant from  $I_e/I_\infty \approx 0.999$ . The thickness of the corresponding sample is called infinite thickness (labeled  $e_\infty$ ) and is defined by  $\rho \mu_m e_\infty \approx 6.9$

If  $D$  is the diameter of the cells used, the minimum volume will be defined by:

$$V_{\min} \approx 6.9 \pi D^2 / 4 \rho \mu_m$$

With  $D = 40\text{mm}$ ,  $\rho = 0.7\text{gcm}^3$  and  $\mu_m \approx 180\text{cm}^2\text{g}^{-1}$  we obtain  $V_{\min} \approx 0.7\text{ml}$ , this result matches the value obtained experimentally with the side effects inside the measuring cell taken into consideration.

#### 4. CALIBRATION

The method that was used is an extension to the one recommended by the ISO/FDIS 20884 standard. Calibration was achieved by using the nett peak intensity of sulfur on the full concentration range spanning from 1ppm to 3%.

The excitation conditions were chosen as 40kV/1.25mA. The integration time was set at two minutes and was also the total time of analysis due to the simultaneous measurement of the two fixed channels.

At the IFP the sulfur analysis in oil industry products used to be carried out on a WDXRF instrument equipped with a 3kW tube. Hence it was important to verify the correlation of results between the two instruments. In order to do this, over two hundred products from various sources, including gasoline, gas oil, vacuum distillates and residues were selected and measured simultaneously with the two instruments. Figures 6 and 7 shown below compare the measured concentrations, for a large variety of samples (up to 3%), on the high power WDXRF instrument and on the WDXRF ARL OPTIM'X. Figure 6 offers a bird's eye view of the low concentration levels (1 to 30ppm range) of the global curve.

This comparison confirms the performance of the ARL OPTIM'X, even at very low concentrations.

#### 5. DETECTION LIMITS AND QUANTIFICATION LIMITS ESTIMATES

A white oil used as blank was measured 10 times consecutively. The estimated standard error calculated from the analyses of this sample is called  $\sigma_c$ . It can ascertain the limits of detection  $L_d$  and the limits of quantification  $L_q$  by defining  $L_d = 6\sigma_c$  et  $L_q = 10\sigma_c$ . The following results were obtained:

	UVF (mg/kg)	ARL OPTIM'X (mg/kg)	Absolute Error) (mg/kg)	Relative Error (%)
Gasoline	1.33	2.0	0.67	50.38
Gas oil	2.79	2.7	0.09	3.23
Coupe 150-250	3	2.0	1	33.33
Pi-80	5.4	6.0	0.6	11.11
Distillate	6.6	5.0	1.6	24.24
Gas oil	7.6	6.3	1.3	17.11

Table 1: Comparison of sulfur determination at levels below 10ppm in various products using UVF and ARL OPTIM'X

$$\sigma_c = 0.22\text{ppm (mg/kg)}$$

$$L_d = 1.3 \text{ ppm (mg/kg)}$$

$$L_q = 2.16\text{ppm (mg/kg)}$$

This quantification limit was tested by analyzing products close to this concentration and the content of which had previously been determined by UVF (ISO 20846 standard). Table 1 indicates the comparison for a series of samples containing very low sulfur concentrations (<10ppm).

#### 6. STANDARDS USED FOR S DOSAGE IN OIL INDUSTRY PRODUCTS

Several standards are available worldwide for the measurement of sulfur in oil industry products. Here we shall only consider the standards currently used or those recommended for analysis of sulfur in gasoline leveling in Europe. Both ASTM D2622-98 and ISO/FDIS 20884 standards recommend the use of wavelength dispersive X-ray fluorescence (WDXRF).

The ISO/FDIS 20884 norm is valid between 5 and 500 ppm. The measurements are carried out at the peak position of  $\text{SK}_\alpha$  and at a slightly different position,  $S_{\text{background}}$ . The difference in intensity between these two measurements (nett intensity) is used for sulfur determination. This norm is one of the two recommended norms European wide for the sulfur determination in vehicle gasoline.

The ASTM D2622 standard uses the following method:

- 10ppm to 1000ppm range : use of the difference in intensity between  $\text{SK}_\alpha$  and  $S_{\text{background}}$  (nett peak)
- Range above 1000ppm : use of the  $\text{SK}_\alpha$  signal (gross peak).

ISO 14596 standard: This norm recommends the use of WDXRF, with a Zr internal standard.

- 1 000ppm to 2.5% range : use of gross peak ratio between  $\text{SK}_\alpha$  and  $\text{ZrL}_\alpha$
- 10ppm to 1000ppm range : use of nett peak ratio between S and Zr

ISO/FDIS 20846 standard: This norm advocates combustion of the sample associated to a UVF detection of the  $\text{SO}_2$  product. This norm is one of two recommended at European level for the sulfur dosage in vehicle fuels.

ISO/FDIS 20847 standard: This norm proposes the use of energy dispersive X-ray

fluorescence (EDXRF). It is valid from 30 to 500 ppm for vehicle fuels.

#### 7. COMPARISON OF THE VARIOUS METHODS

The comparison of the various methods is based on repeatability tests. Several samples covering the 15ppm to 1.5% concentration range were analyzed ten times consecutively with the ARL OPTIM'X using the above described calibration curve. The standard deviation  $\sigma_c$  is estimated for ten measurements at the concentration  $c$  of the sample. The repeatability  $r_c$  is defined by the equation:

$$r_c = 2.8 \sigma_c$$

This repeatability is compared to the maximum values indicated by the different norms mentioned previously, for sulfur concentration ranges in the tested samples below 100ppm and above 100ppm.

It is interesting to note that the instrument shows repeatability in line with the most recent norms for sulfur determination by WDXRF. It is also clear that the repeatability of the ARL OPTIM'X is clearly better to the ISO/FDIS 20847 standard that regulates the use of EDXRF instruments. This last observation is important as these low cost instruments are often deployed in refineries in order to monitor the concentration levels of various elements in oil industry products, but most of them are unable to measure sulfur content lower than 30 ppm.

Long term stability has also been tested by measuring two samples at different levels of concentration. A 22 ppm solution and a 2100 ppm made of white oil and dibenzothiophene have been measured for two months. Results obtained are shown in figure 10 for the two solutions. The excellent standard deviations obtained over a two months period are 0.76 ppm at a sulfur level of 21.8 ppm and 9.45 ppm at a sulfur level of 2102 ppm. For both concentrations, these reproducibility values are well within the ISO 20884 requirements.

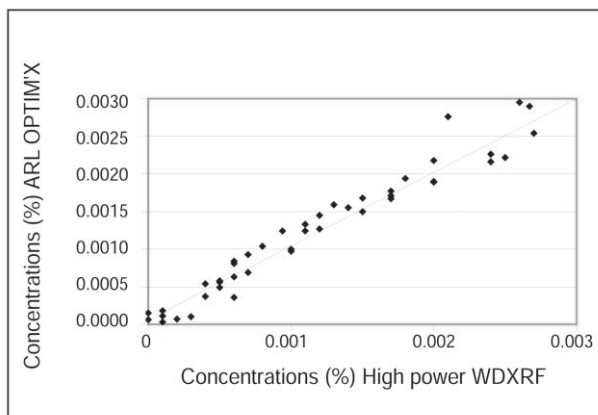
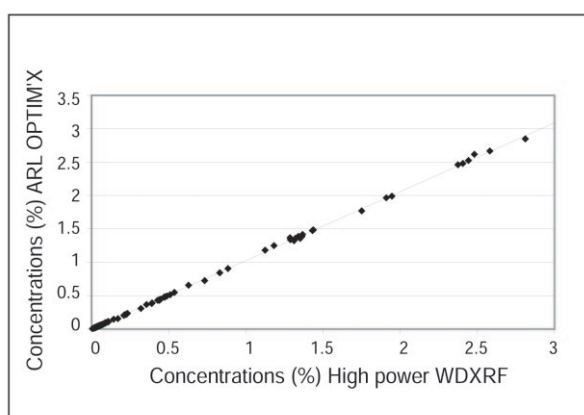


Figure 6 : Sulfur calibration curve from 0 to 3% (ARL OPTIM'X vs. high power WDXRF)

Figure 7 : Detail of the sulfur calibration showing the 1 to 30ppm range.

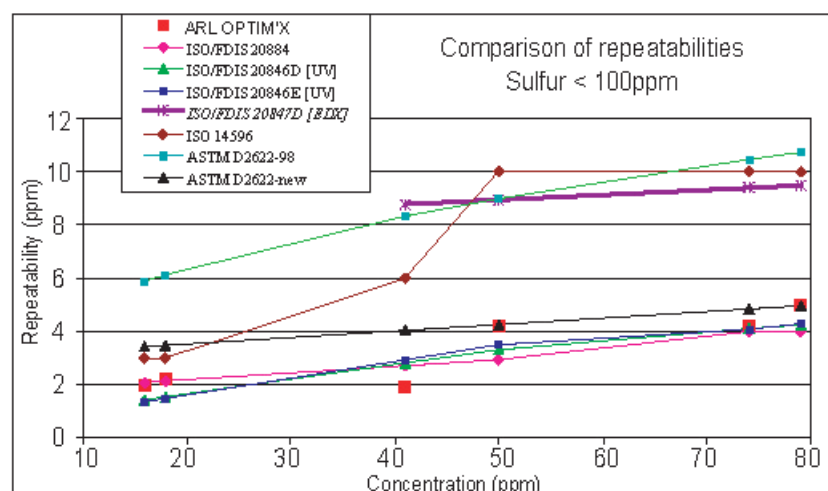


Figure 8: Comparison of repeatabilities for sulfur levels below 100 ppm.

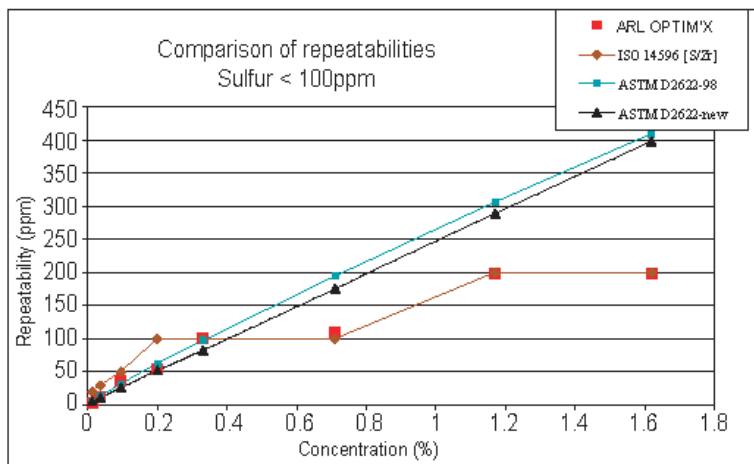


Figure 9: Comparison of repeatabilities for sulfur levels above 100 ppm.

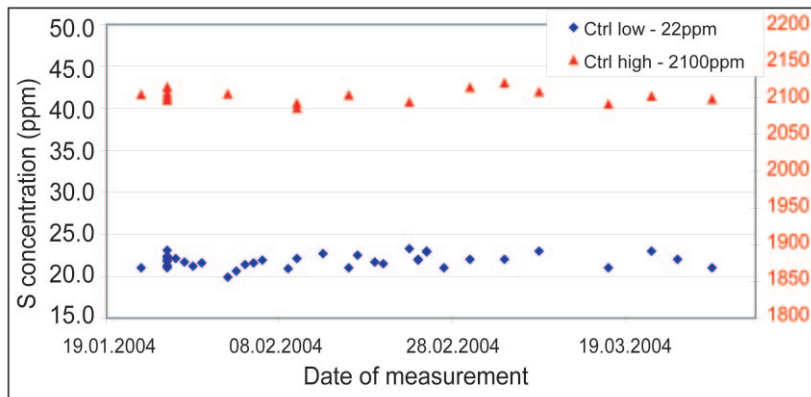


Figure 10: Reproducibility for low and high sulfur analysis over a two months period.

### 8. CONCLUSION

The results of this study have proven extremely encouraging for IFP. They demonstrate the capacity of the entry level WDXRF instrument for routine determination of sulfur in all types of petrochemicals for a very wide range of concentrations. Furthermore the instrument is very easy to use thanks to its touch screen and a specific analytical program. The operator only needs to touch the pre-programmed icon on the screen and the sample identification fields are displayed for information to be entered (sample references, date and time of sampling, pilot unit of origin, operator name). Once the user has validated all this information, the analysis starts. The method established in the IFP laboratory has highlighted the following points:

- a sampling of 2ml is sufficient
- the limit of quantification is about 2ppm with an analysis time of 2 minutes
- the range of determination covers the concentration levels from 2ppm to 3% of S with excellent repeatability and reproducibility (identical or better) compared to most of the reference methods

### Acknowledgments

This paper describes a presentation done at "Rayons X et Matière 2003" and was first published in J.Phys.V, France, EDP Sciences editor. Figure 10 shows new results not yet published.

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