

# Petrochemical products analysis

**Dr Arnd Bühler, Bruker AXS GmbH, Germany, considers the growing trend towards XRF analysis in petrochemical samples, and discusses the merits of the precalibrated OilQuant program.**

**X**RF of solid and liquid petrochemical samples has been used more and more in recent years. An important reason for this trend is the possibility of direct, undiluted analysis of liquid fuels and oils and the relatively simple preparation of samples. Liquid samples can be analysed directly in so called disposable liquid cups, the bottom of which consists of a thin polypropylene, mylar or a similar film (Figure 1). Due to the absorption of the fluorescent radiation in this liquid cup film, a useful liquid analysis via XRF is only possible for elements that are heavier than fluorine (F), from sodium (Na) onwards.

## Instrumentation

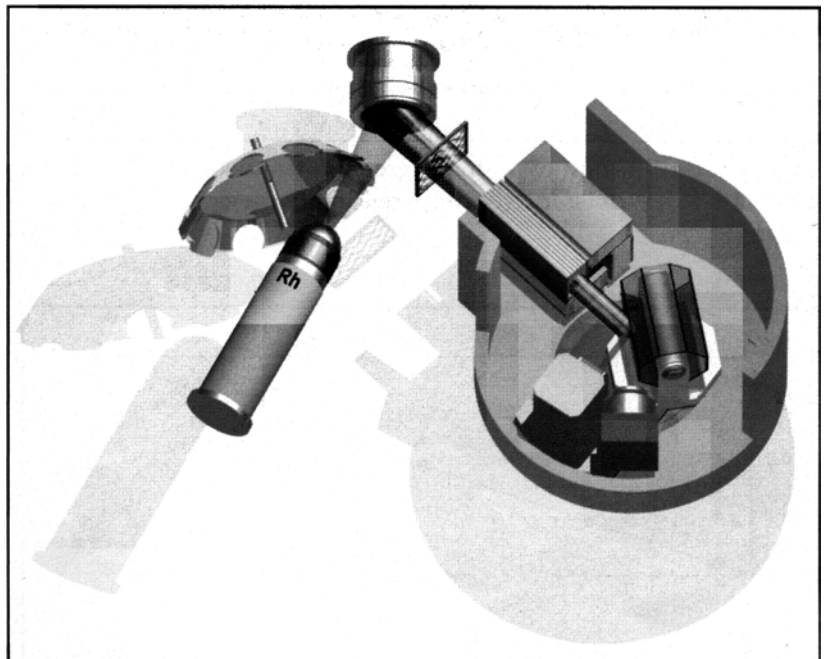
Measurements of solid samples are normally made under vacuum, as the absorption of air renders the analysis of elements that are lighter than Ti impossible. This is not feasible with liquids, which are therefore analysed in a helium or nitrogen atmosphere. In conventional x-ray spectrometers, liquid samples were measured by flush-

ing the complete spectrometer chamber with helium. This had numerous disadvantages. The changing load of the counting tube film when frequently switching between vacuum and helium mode reduced lifetime, particularly of the very thin detector film. Additionally, the counting tube gas that diffused through the detector window into the helium flushed spectrometer chamber was not pumped out, leading to stability problems. Flushing of the overall spectrometer chamber with helium also meant higher helium consumption.

For this reason, modern x-ray spectrometers have introduced a vacuum seal between sample chamber and spectrometer chamber (Figure 2). This computer controlled vacuum seal is automatically inserted during helium operation, separating the evacuated spectrometer chamber with collimators, crystals and detectors from the small sample chamber that is flushed with helium. The very thin and highly transmittant window with supporting grid of the vacuum seal combines a reliable separation



**Figure 1.** Disposable liquid cups for XRF analysis of liquid petrochemical products.



**Figure 2.** In modern x-ray spectrometers, the vacuum seal separates the sample and the spectrometer chamber for safe and economic analysis of liquid fuels.

Table 1. Element and concentration ranges of OilQuant and calibration data						
	Concentration range [µg/g]	Res. dispersion [µg/g]	Sensitivity [Kcps/%]	LLD (3σ; 100 s) [µg/g]	abs. deviation (-25 µg/g; n=15) [µg/g]	abs. deviation (-500 µg/g; n=15) [µg/g]
Na	LLD - 500	7	8.79	7.1	9	9
Mg	LLD - 500	5	17.4	2.8	3	6
Al	LLD - 500	2	14.4	2.0	2	9
Si	LLD - 500	2	11.8	2.3	3	5
P	LLD - 2500	5	11.9	1.4	1	5
S	LLD - 1000	2	17.8	1.1	0.7	4
S	LLD - 5.00%	0.0047%	5.11	2.6	-	0.014% (1.13%)
Cl	LLD - 1000	3	11.2	2.7	4	-
Cl	LLD - 5.00%	0.0040%	1.51	6.0	-	0.020% (1.52%)
K	LLD - 300	2	19.5	1.3	-	-
Ce	LLD - 6000	5	19.2	1.2	1	5
Ti	LLD - 500	1	11.0	1.0	0.6	3
V	LLD - 500	2	27.7	0.8	0.3	5
Cr	LLD - 500	2	32.6	0.8	0.5	6
Mn	LLD - 500	3	36.5	0.7	0.3	3
Fe	LLD - 500	2	18.6	1.0	0.3	3
Ni	LLD - 500	1	18.0	1.0	0.6	3
Cu	LLD - 500	1	21.2	0.9	0.3	3
Zn	LLD - 2500	3	26.6	0.7	0.2	2
Br	LLD - 1000	0.6	41.8	0.7	-	-
Mo	LLD - 500	0.6	27.4	1.9	0.5	4
Ag	LLD - 500	3	1.81	6.0	1	6
Cd	LLD - 500	3	1.54	7.1	2	5
Sn	LLD - 500	4	3.23	3.7	2	4
Ba	LLD - 2000	3	1.68	3.8	1	5
Pb	LLD - 1000	2	7.6	1.2	0.2	3

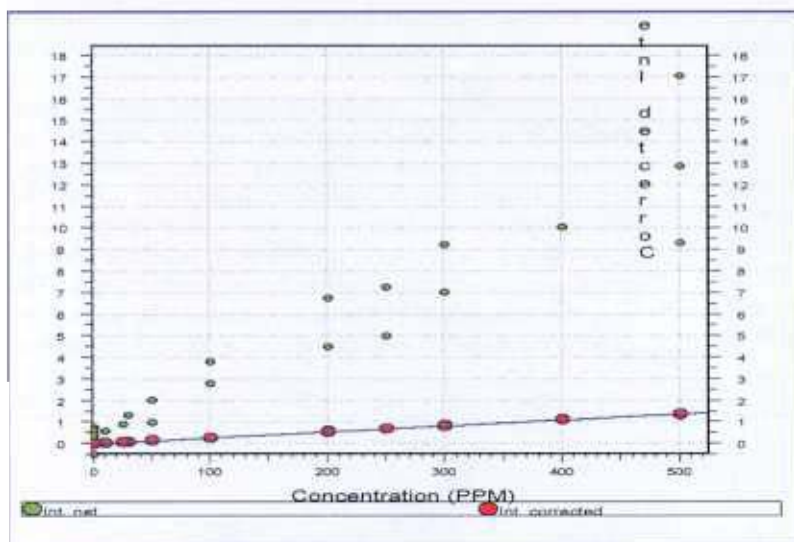


Figure 3. Calibration of V in oil (green dots: uncorrected intensities, red dots: matrix corrected intensities).

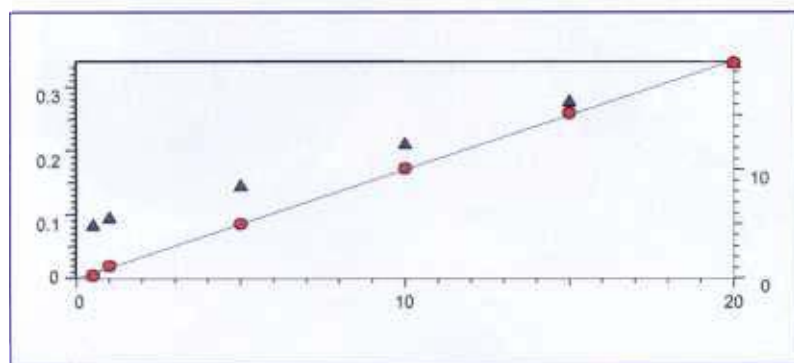


Figure 4. Sulfur calibration for very low concentrations (blue triangles: uncorrected net intensities, red dots: matrix corrected intensities).

with high permeability for radiation. System stability and security are thus increased during measurement and the analytically important physical components (collimators, crystals and detectors) are protected in the separated and evacuated spectrometer chamber. This is also useful for a pure vacuum operation when using contaminated solid samples in certain applications. Additional advantages appear, such as reduced helium consumption, quick mode change (vacuum/helium/vacuum) and minimum absorption of fluorescent radiation, due to the small helium volume in the sample chamber.

## Applications

Improvements in spectrometer technology for liquid analysis were the first step. Simultaneously, the universal precalibrated programs for 'standardless' XRF have been refined and made more efficient for matrix correction by using 'variable alphas'. This resulted, among other things, in the requirement for a specialised, precalibrated program for full quantitative

analysis of petrochemical products, the OilQuant program. Although OilQuant has been optimised for quantitative analysis of liquid fuels and oils, it also offers the possibility of analysing solid petrochemical products, such as greases, resins, polymers and similar substances. The program provides a notable XRF solution to the analysis of alternative liquid and solid fuels.

## Sample preparations

Various preparation parameters of liquid samples influence the results of analysis. These include the inner diameter of the cup, which should be constant; the film material, the selection of which depends on the chemical resistance to the sample material (very important in case of caustic aggressive solutions); the physical stability under x-rays (measuring time) and the tolerable absorption of fluorescent radiation to be measured; as well as the filling height and sample mass. The theoretically analysable layer thickness of hydrocarbons reaches the centimetre range, which is why the deviation from the 'infinitely' thick layer must be considered.

These influence factors have been taken into account in the development of OilQuant, preparing a corresponding preparation guideline. Optimally, the sample quantity is approximately 7.0 g in cups, with an inner diameter of 35 mm, or the cup is filled with the test liquid up to a selected filling height, which is to be maintained continuously. 2.5 µm mylar films were used for gasoline and premium grade gasoline and 4 µm prolene films for diesel fuel and oils. Mylar films have a higher stability and resistance to aggressive solutions than prolene films. However, the latter is characterised by a

higher transmission of fluorescent radiation. Using analysis software, the influence factors of film thickness, film material and impurities (depending on the manufacturer, mylar film is contaminated with Ca, P and low Si or Si contaminated) can be additionally corrected.

## Calibration

Various sets of standard oils from such manufacturers as Conostan (sulfonatic) and Analytical Services (sulfonate-free) were used. They were measured with the S4 Explorer at an excitation of 1000 W (ceramic end window x-ray tube with Rh anode and 75  $\mu\text{m}$  thin tube window). Depending on the element line, the 0.23° or 0.46° collimator was employed and analyser crystals LiF (200), PET and OVO-55. The new, sealed proportional counter Pro4, with a high transmission, was used for light elements and the scintillation counter for heavier elements. Measuring time for peak and background was, for each, 25 s maximum (automatic optimisation via software by counting statistics or maximum time). 'Variable alphas' were used in the Spectra<sup>plus</sup> evaluation software for optimum matrix correction.

The 24 elements that were calibrated ranged from sodium to lead. Two different calibrations are available for sulfur and chlorine, one for trace contents (up to 1000 ppm) and one for contents in the percentage range (>1000 ppm). Table 1 summarises the most important calibration parameters for every element: concentration range, residual dispersion, sensitivity, detection limit and standard repeating deviation for 25  $\mu\text{g/g}$  and 500  $\mu\text{g/g}$  samples.

## Application examples

The potential and accuracy of OilQuant is shown by some calibration examples. Figure 3 represents the calibration of V in oil for the concentration range from the detection limit (0.8  $\mu\text{g/g}$ ) to 500  $\mu\text{g/g}$ . Wider dispersing points above the calibration straight line are net intensities. The points on the calibration straight line are matrix corrected intensities using 'variable alphas'. The corresponding calibration data are listed in Table 2.

A further example is the determination of sulfur in gasoline. During the course of the next few years, sulfur contents of gasoline shall be considerably reduced, below 20  $\mu\text{g/g}$  (possibly below 10  $\mu\text{g/g}$ ) within the EU. This will lead to the definition of corresponding analysis requirements or guidelines. ISO 14596 and ASTM D2622 standards prescribe, for example, the use of wavelength dispersive XRF for sulfur determination in petrochemical products. Figure 4 shows the calibration of sulfur in gasoline for a concentration range from the detection limit (0.4  $\mu\text{g/g}$ ) to 20  $\mu\text{g/g}$ , with a residual dispersion of 0.2  $\mu\text{g/g}$ . The blue triangles represent net intensities, the red dots matrix corrected intensities. This calibration was achieved by refining the OilQuant calibration, using six standards for the lowest concentration range (maintaining the measuring parameters and recalibration measurements, time expenditure: <0.5 h).

Table 3 summarises calibration data for low sulfur concentrations in gasoline and Table 4 comprises the results of a short repetition test. The calibration curve for magnesium in oils is given in Figure 5, along with the corresponding calibration data of Table 5.

Full matrix and preparation correction of advanced XRF software facilitate the use of different preparations for a joint calibration. As already described, besides the preparation with the most transparent (prolene) film, the most important preparation to be named is the one with the chemically more stable film (mylar). Table 6 states analytical results of using various films in the disposable liquid cup

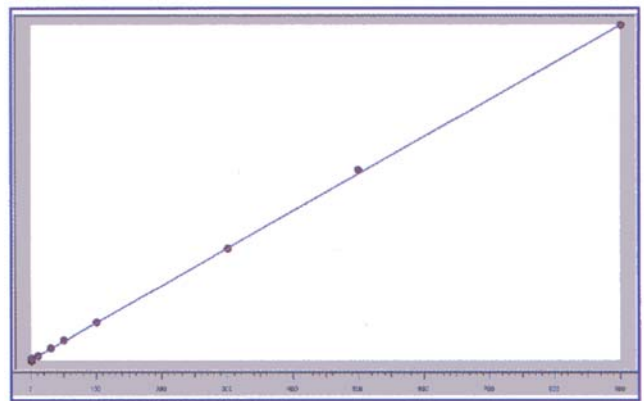


Figure 5. Calibration of magnesium in oils (standard deviation of calibration is 3.2 ppm).

Table 2. Calibration data of V in oil

Standard	Certified conc. [ $\mu\text{g/g}$ ]	XRF conc. [ $\mu\text{g/g}$ ]	Abs. dev. [ $\mu\text{g/g}$ ]	LLD [ $\mu\text{g/g}$ ] (3 s; 100 s)
SNVMO12-11	500.0	499.8	0.2	1.9
SNVMO12-02	500.0	499.8	0.2	1.8
S21-500	500.0	492.8	7.2	1.8
SNVMO12-06	400.0	401.3	1.3	1.6
SNVMO12-07	300.0	297.8	2.2	1.4
S21-300	300.0	305.9	5.9	1.5
SNVMO12-10	250.0	251.6	1.6	1.4
SNVMO12-04	250.0	248.2	1.8	1.4
SNVMO12-08	200.0	200.9	0.9	1.2
S21-200	200.0	206.0	6.0	1.2
SNVMO12-05	100.0	99.7	0.3	1.0
S21-100	100.0	105.1	5.1	0.9
SNVMO12-12	50.0	50.7	0.7	1.3
S21-050	50.0	51.5	1.5	0.8
S21-030	30.0	31.3	1.3	0.8
SNVMO12-03	25.0	24.2	0.8	0.9
S21-010	10.0	10.9	0.9	0.8
SNVMO12-09	0.0	0.7	0.7	1.1
SNVMO12-01	0.0	-0.6	-0.6	0.8

Table 3. Calibration data of sulfur in gasoline

Standard [ $\mu\text{g/g}$ ]	Certified concentr.	XRF concentr. [ $\mu\text{g/g}$ ]	Abs. deviation n [ $\mu\text{g/g}$ ]	LLD [ $\mu\text{g/g}$ ] (3 s; 100 s)
Gasoline 1	0.0	0.5	-0.2	0.4
Gasoline 2	1.0	1.1	0.1	0.4
Gasoline 3	5.0	5.0	0.0	0.4
Gasoline 4	10.0	10.1	0.1	0.4
Gasoline 5	15.0	15.2	0.2	0.4
Gasoline 6	20.0	19.8	-0.2	0.4

Table 4. Repetition measurements of sulfur in gasoline

	Gasoline 2 ( $\mu\text{g/g}$ )	Gasoline 3 ( $\mu\text{g/g}$ )
Standard	1.1	5.0
1 <sup>st</sup> repetition	0.8	4.8
2 <sup>nd</sup> repetition	1.0	4.7
3 <sup>rd</sup> repetition	0.9	5.0

and different sample volumes.

The film material used (prolene, polypropylene and mylar) and filling height were varied in this analysis. It can be seen from the element values of P onwards that a notable overall analysis is obtained, independent of the film used. Film contaminations are automatically compensated by measuring so called blank samples (depending

on the preparation/film, a technical white oil in a suitably covered cup). Very light elements such as Mg show, however, a slight dependence on the film. In this case, it has to be taken into account that the absorption of a thin mylar film reduces the measured intensities of the elements Na and Mg by approximately one order of magnitude, so that even small values/errors are multiplied with a large correction factor.

**Table 5. Calibration data for magnesium in oils**

Standard	Certified concentration [µg/g]	XRF concentration [µg/g]	Abs. deviation n, [µg/g]	LLD [µg/g] (3 s; 100 s)
Gasoline 1	900.0	896.4	-3.6	5.0
Gasoline 2	500.0	508.3	8.3	4.5
Gasoline 3	300.0	296.5	-3.5	4.1
Gasoline 4	100.0	99.2	-0.8	3.7
Gasoline 5	50.0	51.5	1.5	3.6
Gasoline 6	30.0	30.8	0.8	3.6
Gasoline 7	10.0	9.2	-0.8	3.4

**Table 6. Analysis results of various preparations**

Preparation	Mg [µg/g]	P [µg/g]	Cl [µg/g]	Ca [µg/g]	V [µg/g]	Zn [µg/g]	Pb [µg/g]
4 µm prolens, 7.0 ±0.1g	237	270	255	275	292.6	288.3	303.6
5 µm polyprop., 7.0 ±0.1g	251	266	255	273	284.7	282.4	295.8
2.5 µm mylar, 7.0 ±0.1g	295	273	249	271	278.1	269.0	283.0
2.5 µm mylar, 2.5, 0 ±0.1g	282	275	238	275	284.9	297.0	316.6
2.5 µm mylar, 5g, 0 ±0.1	281	273	244	270	282.5	277.8	296.8
2.5 µm mylar, 10g, 0 ±0.1	283	273	246	267	278.6	265.3	271.8

## Conclusion

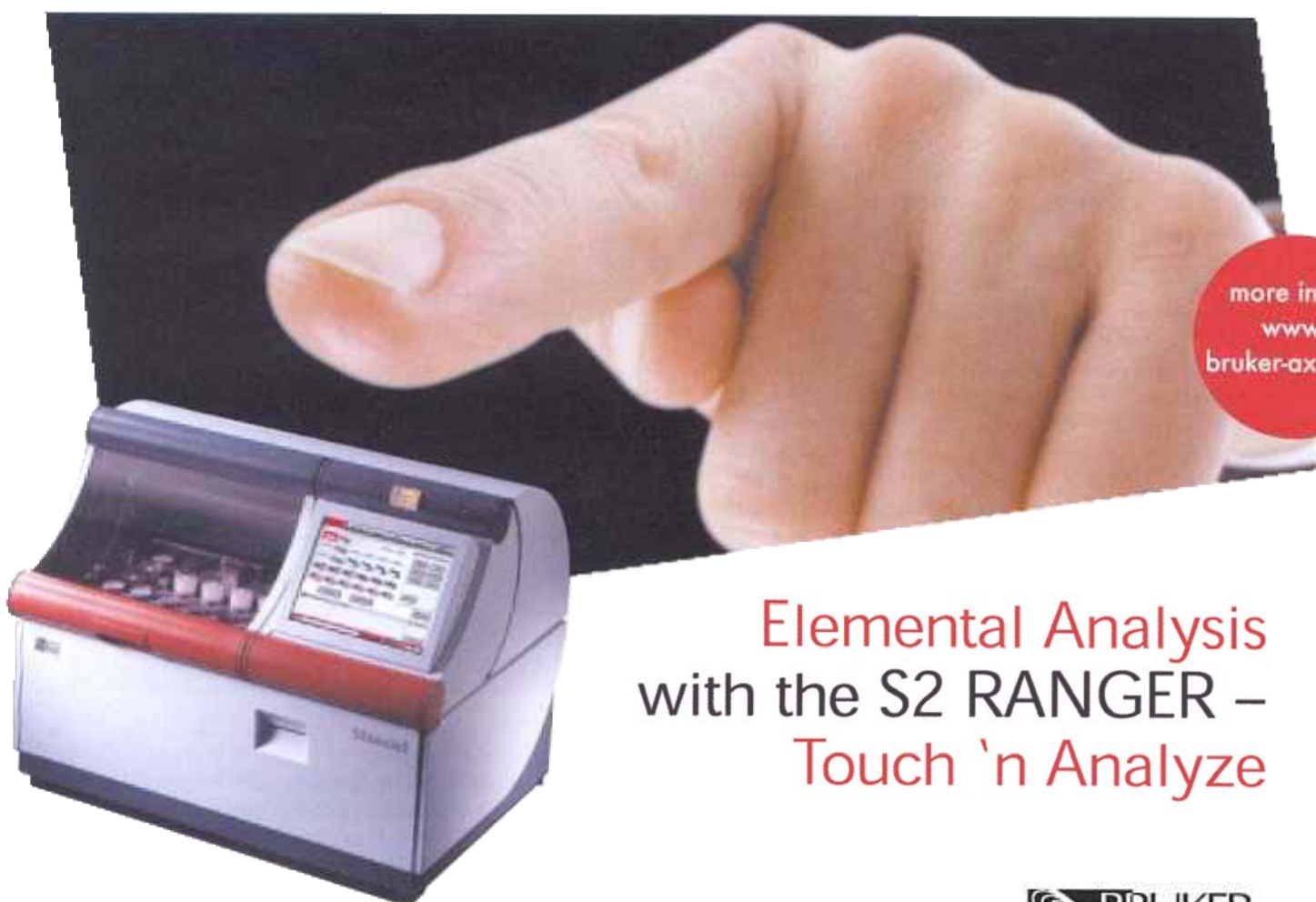
In x-ray fluorescence analysis, functionality and quality of software have reached a very high level in recent years. In the meantime, the following have become a matter of course:

- Quick and simple configuration of analytical programs.
- Easy and reliable device control.
- A large variety of evaluation procedures and correction models for quantitative analysis.
- Calculation of fundamental parameter coefficients ('theoretical or variable alphas') for effective matrix corrections.
- Flexible graphic representation and automatic element identification in qualitative analysis.
- Universal and flexible lab network integration of the analytic system.
- Fast, secure data transmission.

Pre-calibrated programs for full quantitative multi element analysis are a further important step in this development. One example is the use of the precalibrated OilQuant program for a simple and flexible full quantitative determination of the most important minor and trace elements in liquid petrochemical products for different preparations. In addition to the ASTM, ISO etc. standards, OilQuant supports daily analytical routine in any petrochemical process and quality control or R&D laboratory.

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