

XRF Fundamentals



Introduction

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2 Introduction

XRF is becoming the universal tool in analytical laboratories...

The traditional use of XRF has its roots in geology. Solid samples were the first sample types analyzed by x-rays. More and more, XRF is becoming the universal tool in analytical laboratories including applications traditionally handled using atomic absorption spectroscopy (AAS) or inductively coupled plasma-optical emission spectroscopy (ICP-OES). There is virtually no industry or application field where it isn't worthwhile to consider the use of the XRF analysis technique. The advantages are clear: easy sample preparation, multi-element determination, and the possibility to screen completely unknown samples.

2.1 Which elements can be analyzed?

With XRF all elements between Na and U can be analyzed. For the elements from Na to Ce K-lines are used, and for all elements from Pr to U, L-lines are used.

The analysis of the elements Be to F is limited to just a few special applications. The reason for this is the depth of analysis. These elements show low energy x-rays that are easily absorbed by air or a simple polypropylene film.

With XRF all elements between Na and U can be analyzed.

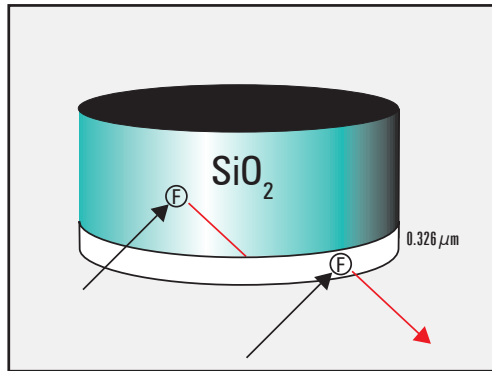
Element	Application	Remark
B	B in wafers	Only WDXRF, polished surface
C	C in steel	Only WDXRF, sample must be re-melted before measurement to avoid inhomogeneities
F	F in polymers	Only special detectors with HT window (cannot measure powders).
Be-F	Liquids, powders in sample cups	Not possible with XRF. Lines are absorbed in the film which covers the bottom of the cup
Na, Mg	Liquids, powders, pellets, fusions	Only with He-purge or vacuum (pellets + fusion)
F -Cl	All	Depth of analysis is very shallow, particle size must be $\sim 60 \mu\text{m}$, sample must be extremely homogeneous
K-U	All	With increasing atomic number particle size, effects decrease and penetration of the sample increases.

Table 1: Overview of elements detectable with XRF.

Pressed Pellet

Penetration Depth	
F	0.326 μm
O	0.305 μm
N	0.29 μm
C	0.136 μm
B	0.06 μm
Be	0.045 μm

Figure 1: Penetration depth of x-rays for light elements.



To get reproducible results, you need a grain size of $0.02 \mu\text{m}$. This is not achievable!

Loose Powder and Liquid

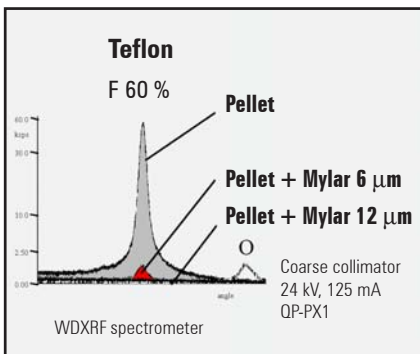


Figure 2: Measurement of fluorine. Absorbance of fluorine intensity by films covering the bottom of the sample cup. The main reason why fluorine cannot be measured in a sample cup.

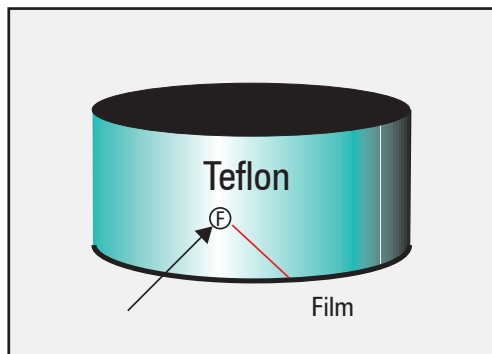
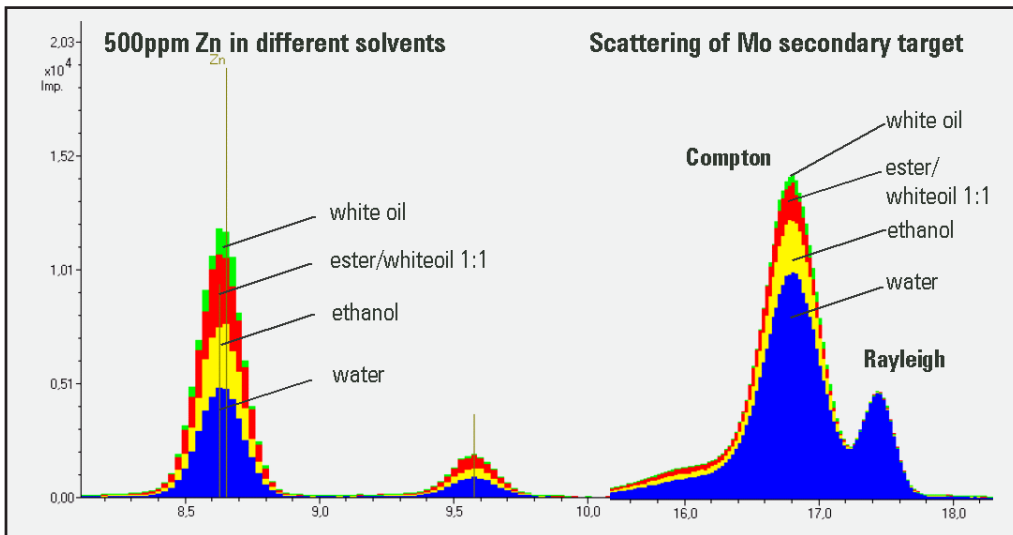


Figure 4:
Each solvent shows a different absorption of x-rays. The Mo radiation from the Mo secondary target used for excitation is scattered at the sample. Also the scattering shows matrix dependence. This can be used for matrix correction (e.g. in TURBOQUANT).



In general, matrix effects occur when one component of the sample changes its concentration by more than 0.5 %.

The biggest advantage of XRF is its easy sample preparation, especially for solid samples where collection for a sample cup or even making pressed pellets is less work than a digestion for ICP-OES or AAS. It is well known that one type of digestion is not effective for all elements between Na and U. Another disadvantage of a digestion is the small sample amount, generally less than 0.5 g. For XRF samples, quantities between 3 and 8 g are typical. This is very important for inhomogeneous samples where more sample material reduces the influence of the inhomogeneity.

Disadvantages of the analysis of solids with XRF are the associated matrix effects. To get a correct analysis, these effects need to be taken into account and corrected. Selecting a special type of sample preparation can do this, but this is usually accomplished by describing the fluorescence process, theoretically, using fundamental parameters. The excitation process as well as the detection of a fluorescence line is always performed in the same constant manner. To describe it completely, the geometry of the x-ray beams has to be known, as well as the characteristics of the x-ray tube, target and detector. The behavior of the tube, target, detector, and the geometry must always be the same. The penetration depth of the x-rays into the material is found in tables stated as mass absorption coefficient and can be calculated for each element. The software knows all of these parameters; therefore, it is possible to describe the XRF analysis theoretically.

The importance of detector resolution

There are different types of detectors used in EDXRF. The differences in detection systems can be seen from different spectral resolution, from the pulse throughput and the absorption characteristics for X-Rays. Some of the detection systems require cooling with liquid nitrogen, others are electrically cooled or do not require any cooling at all.

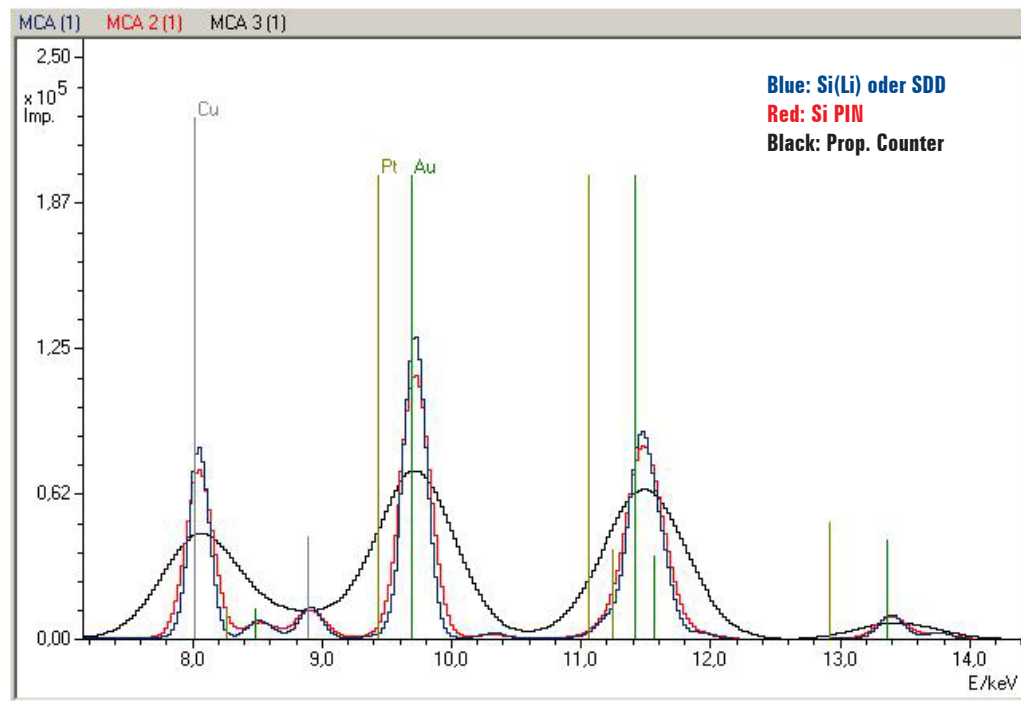
2.3

Currently there are four different types of detectors used in EDXRF.

For any given application, it is important to choose the right detector.

In Figure 5, the resolution of the different detection systems are shown for the Mn K lines. The proportional counter detector (PC) is not able to resolve neighboring elements' lines. The Silicon PIN-diode shows a much better resolution than the PC and is able to resolve neighboring elements. A Silicon drift detector (SDD) achieves a better resolution than the two previous mentioned systems. The essential advantage of SDD's is the highest available count rate throughput, which can lead to better precision of the analysis or shorter measuring times. Detection systems cooled with liquid nitrogen achieve a very good resolution, too. This can have additional benefits for the absorption of some high-energy X-Rays.

For any given application, it is important to choose the right detector. If only one element has to be detected, and it won't be overlapped by other elements, resolution is not important, only sensitivity is. In this case one may choose a PC. In the same situation where neighboring elements have to be resolved, a semi-conductor detector is required. Here it is important to consider if we are just looking for traces or if we want to analyze traces and main components. In such a case only a Silicon drift detector or Si(Li) detector can do the job.



2.4 Why use polarization?

The main reason for using polarization is to improve analytical sensitivities. This leads to a better peak to background ratio and therefore better sensitivity.

The main reason for using polarization is to reduce the spectral background.

In classical EDXRF and in WDXRF, direct excitation is used. These techniques suffer from a high spectral background which is a result of the excitation x-ray scatter. In EDXRF bad peak to background ratios are the result. In WDXRF the problem is overcome by using high power x-ray tubes - up to 4 kW - that require water-cooling.

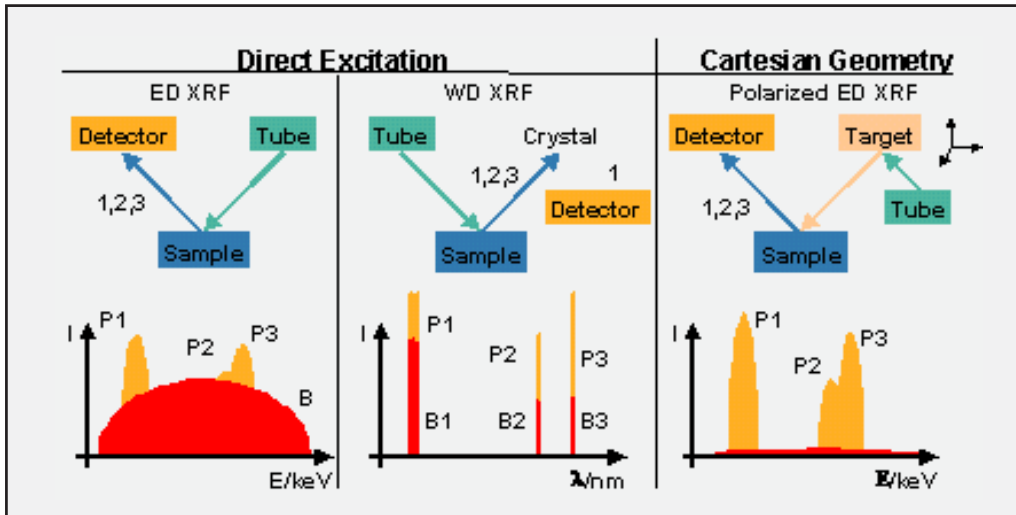


Figure 6: Different XRF techniques: EDXRF, WDXRF with direct excitation and EDXRF with polarized excitation: EDPXRF.

To polarize x-rays you need a certain geometry: tube, target, sample and detector must be arranged in a Cartesian geometry. Polarization is performed by changing the direction of x-rays by 90°. However, it is not important which physical process is involved in polarizing x-rays. The x-rays coming out of the tube are reflected or scattered by the target with an angle of 90° to the sample; this means that the non-polarized x-rays from the tube are polarized at the target. Then the polarization plane is the same as for the target, sample, and detector. Once these polarized x-rays hit the sample, it can only be scattered orthogonal to the plane and because the detector is placed inside the plane, it can only detect the fluorescence radiation coming from the elements in the sample.

Polarization is performed by changing the direction of x-rays by 90°.

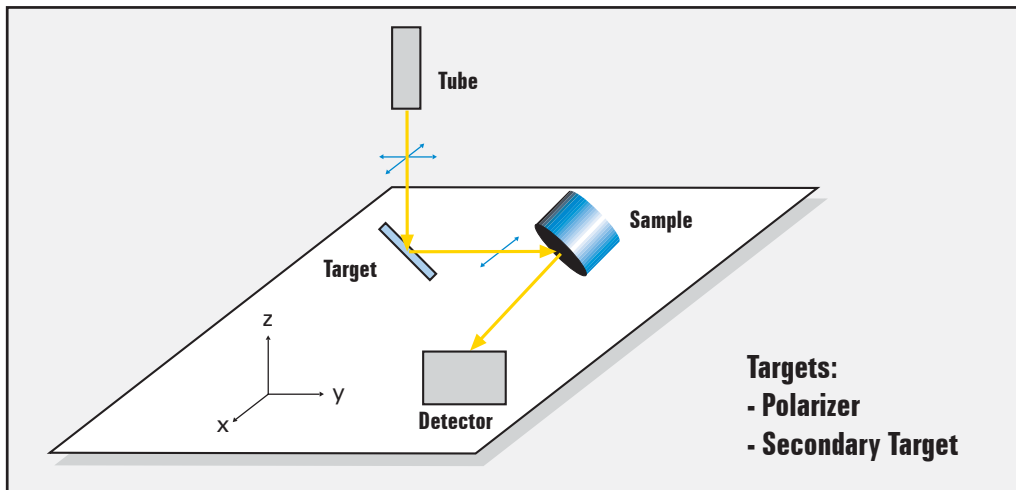


Figure 7: Cartesian geometry for polarization of exciting x-rays.

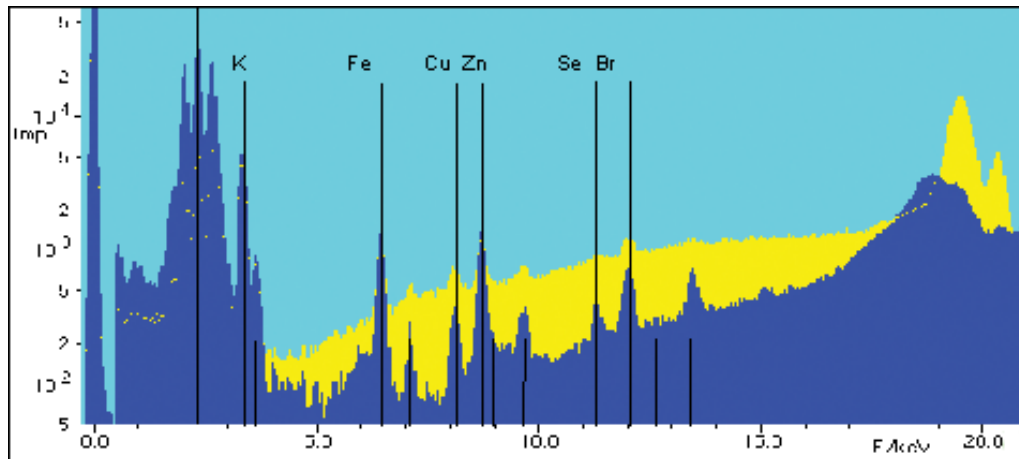


Figure 8: Comparison of spectra of certified reference material (BCR-186) with direct excitation (yellow) and polarized radiation (blue).

...background is the scattering of the exciting x-rays at the sample.

Figure 8 shows the comparison between direct and polarized excitation. Both spectra are normalized to the height of Fe and Zn. This gives a good impression of how the peak to background ratio improves when background is reduced and the reduction is compensated by higher fluorescence lines due to polarization.

Polarization will always show a big improvement over the classical direct excitation when the spectrum exhibits a high background. To understand now how polarization will improve the analysis, the reasons for spectral background have to be understood.

One of the main causes for background is the scattering of the exciting x-rays at the sample. Heavy sample materials, like alloys, show virtually no scattering, which means polarization won't give an advantage. Light sample materials, like organics, polymers, liquids, silicates and even a lot of minerals generate a high level of scattering. These are the applications where the polarization technique performs best and generates the highest sensitivities in XRF.

Sample Preparation

3

Importance of sample preparation

3.1

The error of the analysis goes along with the sample preparation, i.e., the error of the sample preparation must be in agreement with the required precision of the analytical method. The available preparation techniques for solids are powder or pressed pellets. In particular, the error of the light elements Na to Cl decreases by using pressed pellets in the preparation technique. For liquids, simply pouring into a sample cup is acceptable.

The error of the analysis goes along with the sample preparation...

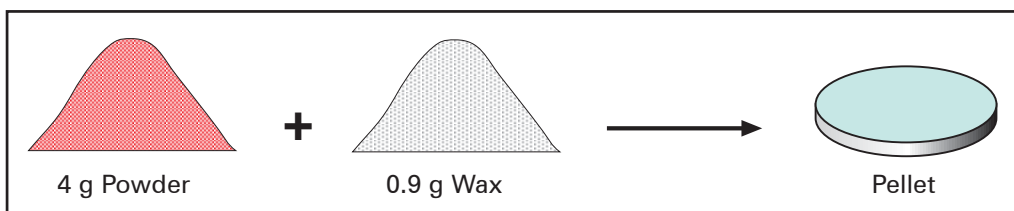
Solid

3.2

Pellets

3.2.1

4 g of a powder ($< 100 \mu\text{m}$) is mixed well, homogenized with 0.9 g of Clariant micropowder C, and then pressed with 15 tons to pellet with 32 mm diameter.

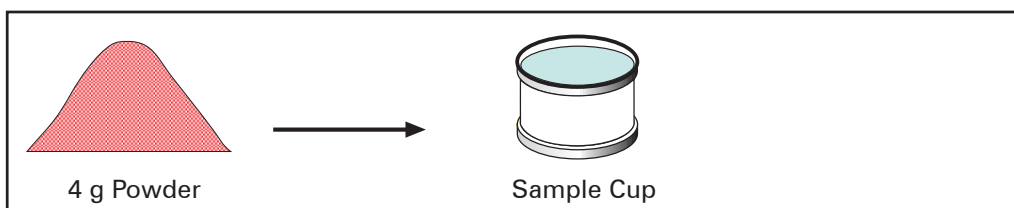


Sample:	Powder
Additives:	Clariant micropowder C
Preparation Utilities:	Mill Container for grinding and mixing Die (diameter 32 or 40 mm) Press min. 15 ton

Powders

3.2.2

4 g of a powder ground down to $< 100 \mu\text{m}$ is poured into a sample cup with an inner diameter of 28 mm. The bottom of the sample cup is covered typically with a 4 μm polypropylene film. After pouring, the powder will be slightly pressed with a pistil to form a good surface to avoid any air holes on the bottom.

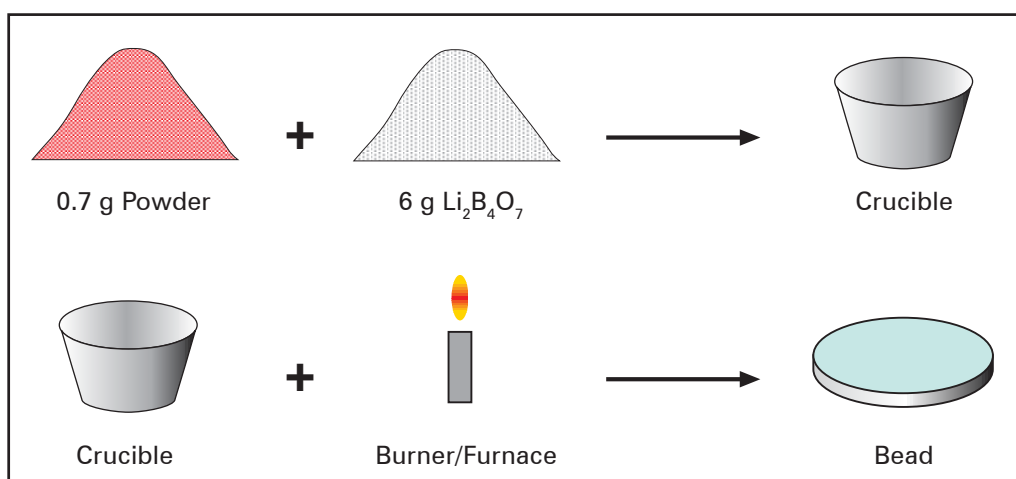


Sample:	Powder
Additives:	None
Preparation Utilities:	Mill for grinding sample cups (outer diameter 32 or 40 mm) Polypropylene foil 4 μm thickness Pistil

3.2.3 Fusions

The sample material must be dried and milled to a grain size lower than $100\ \mu\text{m}$. 0.7 g of the powder is homogenized with 6.0 g of Flux and then fused at 1100°C to a 40 mm bead. As a standard procedure, a 10-minute fusion time should be sufficient. The flux should be selected carefully in order to create a completely dissolved sample in the fused bead. Depending on the material and the fusion machine, time and temperature may vary. For some materials a pre-oxidation may be necessary.

In some cases it is necessary to reduce the sample amount down to 0.2 g. If a lot of fusion remains in the crucible, the use of a wetting agent (e.g. NH_4I) may be required.



Sample:	Powder
Additives:	Flux, wetting agent
Preparation Utilities:	Platinum/gold crucible and mould Fusion machine or furnace



There are some materials that may destroy your Pt/Au crucible. The most dangerous for the Pt/Au crucibles are metals, especially elemental silicon, boron, or iron; carbides are also dangerous.

Liquid

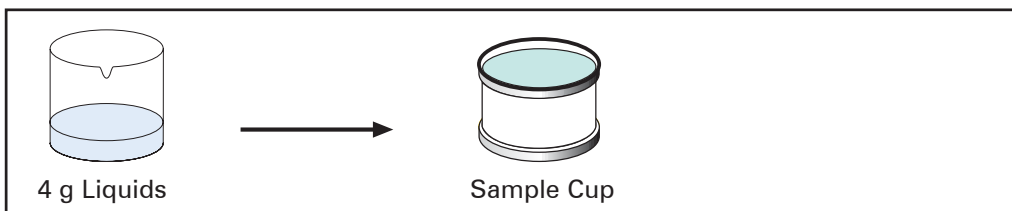
3.3

Monophased / Polyphased

3.3.1

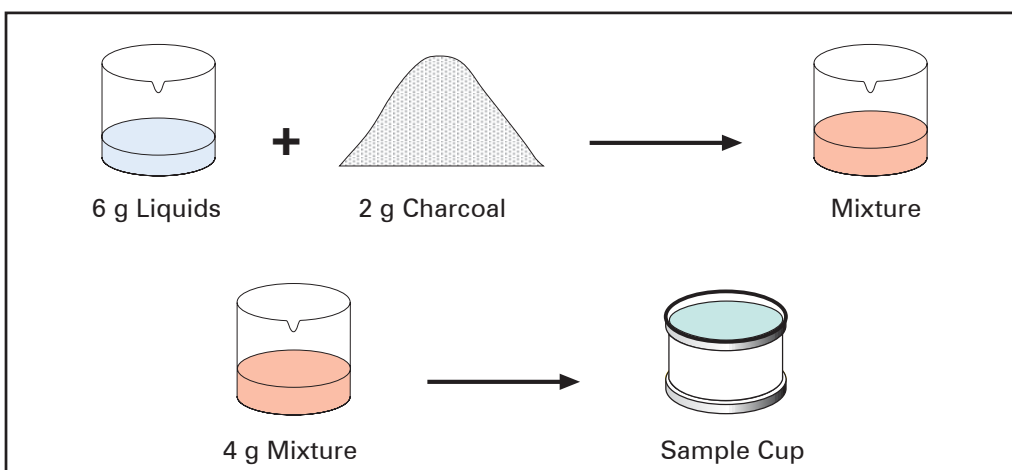
4 g of a liquid is poured into a sample cup with an outer diameter of 32 mm. The bottom of the sample cup is covered with a 4 μm polypropylene film.

Monophased Liquids:



Polyphased Liquids:

To analyze polyphased liquids (liquid / liquid or solid / liquid) or highly volatile liquids, it is advised to use 4 g of a well-homogenized mixture prepared using 6 g sample and 2 g charcoal (Merck).



Sample:	Liquid: oil based, water based, polyphased liquids
Additives:	None, charcoal for polyphased liquids
Preparation Utilities:	Sample cups (outer diameter 32 or 40 mm) Prolene foil 4 μm thickness Mixing containers for polyphased liquids

Accessories

3.4

Mill

3.4.1

For preparation of pellets or loose powder, it is very important that the particle size is < 100 μm . To mill the samples, the use of a mill is quite common. Also it is recommended to use a Zirconium dioxide grinder (volume 25 ml good for 10 g of material) Zirconium dioxide is hard enough to grind most all materials. The TURBOQUANT programs need powder and pellet samples prepared to < 100 μm !

For preparation of pellets or loose powder, it is very important that the particle size is < 100 μm .



Figure 9:
Mill with a ZrO_2
grinding vessel
for grinding of up
to 10 g.

To grind larger amounts of sample material (up to 60 g), a disc vibration grinding mill is recommended.



Figure 10:
Mill with an Al_2O_3
grinding vessel
for grinding of up
to 60 g.

3.4.1

Press

For preparation of pellets, a press with a pressure up to 15 tons is sufficient



Figure 11:
Manual press up
to 15 tons.



Figure 12: Example for different types of dies.

3.4.3

Die

To prepare pellets, you need a die. The powder is homogenized with the wax using a mixing container in the mill MM2. The mixture is then poured into the die and pressed with 15 tons.

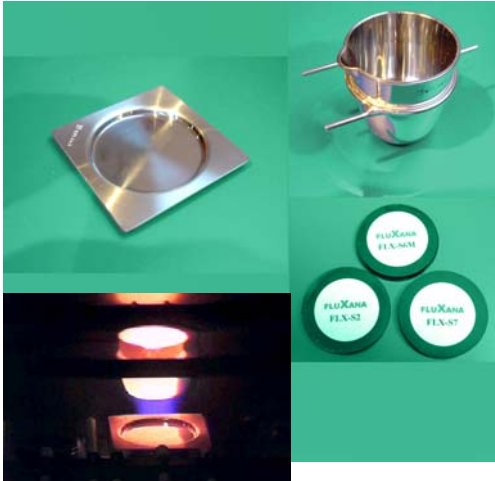


Figure 13: Fusion Machine (2 burners, also available with 4 burners).

3.4.4

Fusion Machine

Fused beads give the most accurate results for those elements which suffer from grain size effects on their fluorescence radiation. To make the preparation procedure as easy as possible, one may use the 2 burners or 4 burners fusion machine. This machine fuses samples fully automatically. The sample is weighed into the Platinum crucible together with the flux, and then the crucible is placed into the fusion machine. Program 1 will dry the sample. Program 2 melts the flux + sample. Program 3 stirs the melt, and program 4 pours it into the pre-heated mould. The bead then cooled and can be used for analysis.



3.4.5

Chemicals

- | | |
|------------------------|--------------------|
| Clariant micropowder C | Pellets |
| Charcoal (Merck) | Polyphased liquids |
| Flux | Fused beads |

4 Calibration Methods

4.1 TURBOQUANT

TURBOQUANT is able to analyze the elements from Na to U in completely unknown samples.

TURBOQUANT is the brand name for a SPECTRO method that is used for screening analysis. The method is able to analyze the elements from Na to U in completely unknown samples. This means that all matrix effects which will occur are taken into account. The only distinction is made between solids, liquids and alloys (there is a separate program for each). With this highly flexible mode, the accuracy is between 10 to 20 % relative. Whenever it is possible to limit the possible matrices, i.e., only for organic matrices, the relative accuracy can be improved.

The excitation of all elements (Na-U) is split into three single measurements using different targets. The light elements Na-V are excited using a HOPG target (intense monochromatic polarized x-rays). The elements Cr-Zr and Pr-U are excited using a Mo secondary target (intense monochromatic non polarized x-rays). The high-energy elements Y-Ce are excited using a Barkla Al_2O_3 target (intense polychromatic polarized x-rays).

Target	Type of Target	Excited Elements
Mo	secondary	Cr - Y (K), Pr - U (L)
Al_2O_3	Barkla	Zr - Ce
HOPG	Bragg	Na - V

Table 2:
Targets and
Corresponding
Elements in
TURBOQUANT.

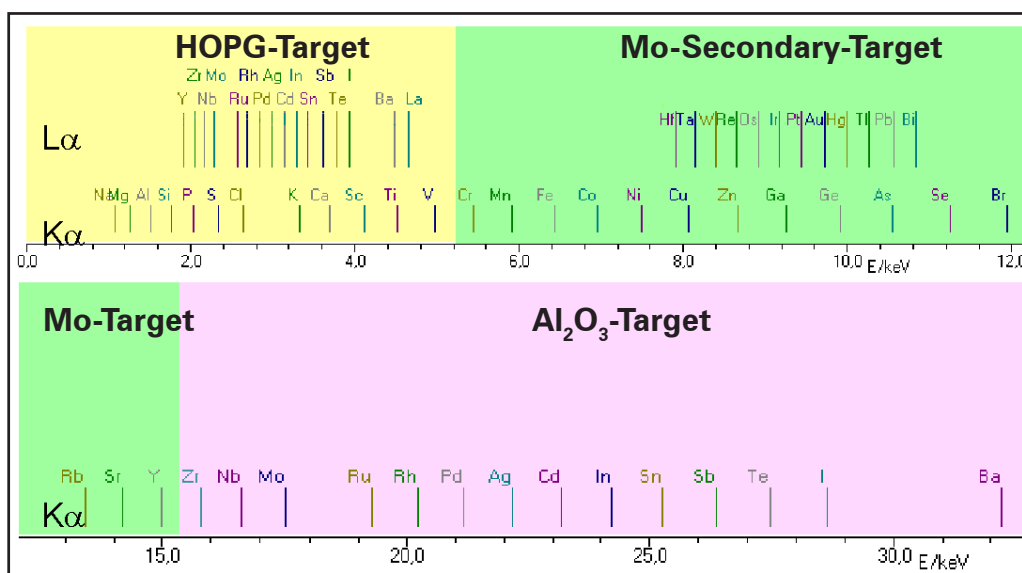
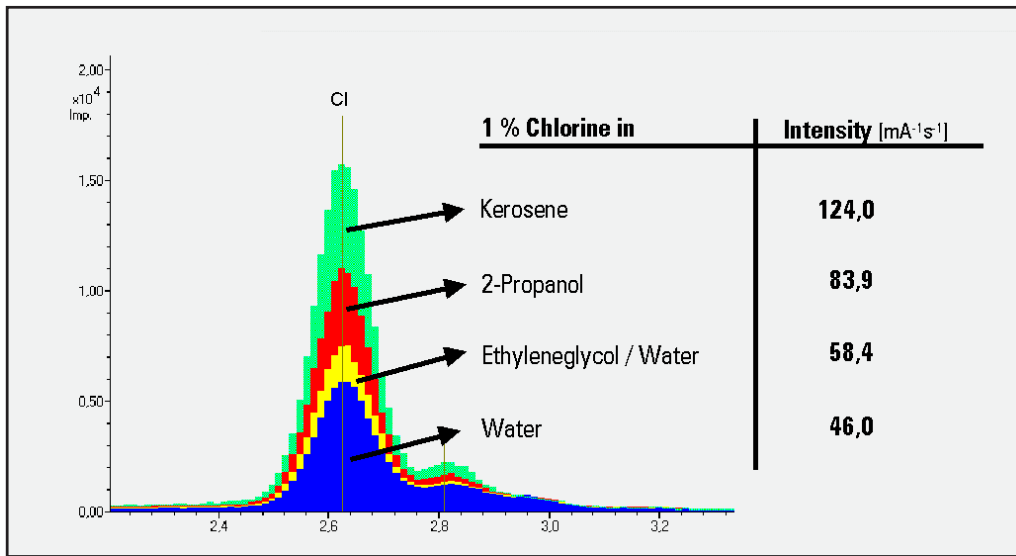


Figure 14:
Excitation of K
and L lines with
different targets.

Four solutions of 1 % Chlorine were prepared with 4 different solvents: water, ethylene glycol / water (86 % / 14 %), 2-propanol, and kerosene. The detected intensities show a difference between water and kerosene of a factor 2.7. This is caused by the variation of the oxygen and carbon contents in the liquids. The calculation of the theoretical mass absorption coefficients for 2.6 keV gives a factor of 2.6.

One of the main features of TURBOQUANT is the automatic matrix correction.

Figure 15: Influence of different matrices on the intensity of the chlorine K α -line. Measurement was done using a HOPG-target, 10 kV, 200 s.



To handle different matrices with one calibration, the intensities first have to be corrected for the matrix effect. This can be accomplished using the well-known Compton Method (One may understand that this line is used as internal standard). This method is based on the fact that all elements contained in a sample contribute to the Compton scattering of the excitation radiation. That means the intensity of the Compton peak is related to the mass absorption coefficient of the specimen. This can be used for an unknown sample to calculate the mass absorption coefficient based on the Compton peak and then the intensities of the element lines are subsequently corrected based on the mass absorption (this is valid for liquids and solids).

For calibration, a Fundamental Parameter (FP) approach is used. Based on the corrected intensities for each element, the correlation between intensity and concentration is calculated. The main advantage of FP versus empirical methods is its capacity to take into account all possible inferences between the elements.

This evaluation technique is used for solid and liquid samples.

4.1.1 TURBOQUANT for liquids

The use of an automatic matrix correction makes it possible to analyze liquids of different origins with the same calibration. For example, water and oil based samples can be analyzed in the same way as solvents or even polyphased liquids. For an optimum calibration, a special set of standards, containing ICP standards (Merck, Bernd Kraft) and oil standards (Conostan) were used. Fig. 16 demonstrates the performance of the method for the analysis of halogens over a large concentration range from 10 $\mu\text{g/g}$ to 10 %. It is possible to extend the calibration range for Cl up to 80 %.

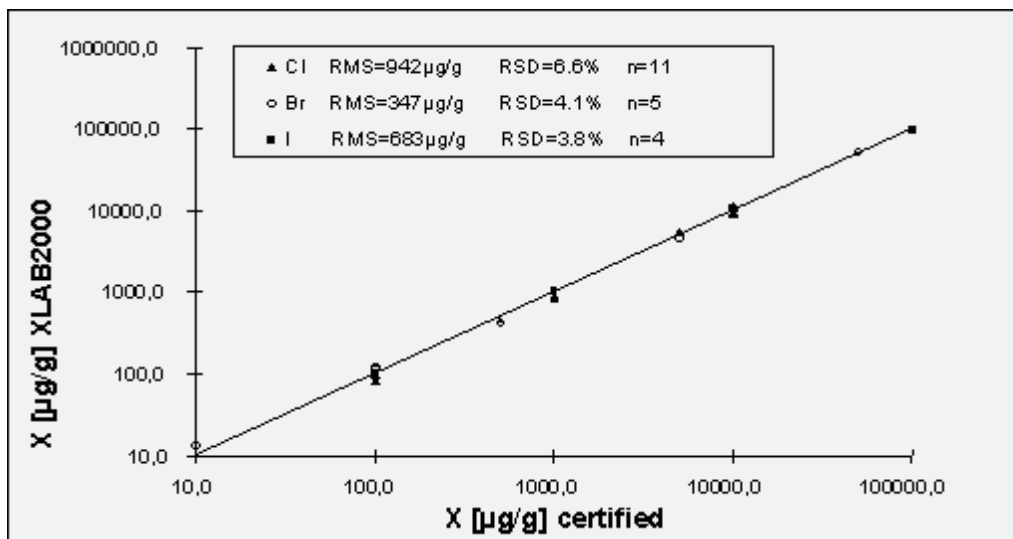


Figure 16: Calibration of halogens in liquids with TURBOQUANT. Measurement time 200 s.

1% Chlorine in	Kerosene	2-Propanol	Ethyl.glicol / Water	Water
TURBOQUANT[%]	1.01	1.05	0.88	0.98

Table 3: Results of TURBOQUANT liquid for Cl in different solvents.

Element	SPECTRO X-LAB 2000 Conc. [$\mu\text{g/g}$]	Known Conc. [$\mu\text{g/g}$]
Cr	21	27.5
Mn	30	17.5
Fe	<100*	22.5
Co	10	10
Ni	35.5	40
Cu	28.8	25
Zn	27	25
Ga	55	75
Ag	39	40
Cd	21	25
Pb	104	115

*Impurity of charcoal

Table 4: Results of a polyphased sample, total measurement time 600 s, 3 g sample + 1 g charcoal as absorbing material.

Element	Average Value (n=3)	certified Value
Cl	6.49 ± 0.04 %	(6.5 %)*
Ti	104 ± 18 µg/g	125 µg/g
Cr	117 ± 3 µg/g	125 µg/g
Mn	120 ± 4 µg/g	125 µg/g
Fe	120 ± 17 µg/g	125 µg/g
Co	122 ± 14 µg/g	125 µg/g
Ni	116 ± 7 µg/g	125 µg/g
Cu	135 ± 4 µg/g	125 µg/g
Zn	125 ± 3 µg/g	125 µg/g
Sr	123 ± 2 µg/g	125 µg/g
Cd	116 ± 3 µg/g	125 µg/g
Ba	121 ± 3 µg/g	125 µg/g
La	120 ± 2 µg/g	125 µg/g

(*Value in brackets are not certified)

Table 5: Reproducibility of an ICP multi-element standard prepared 3 times with charcoal (3 g sample + 1 g charcoal).

TURBOQUANT for pellets/powder/metals

A matrix correction is done for solids in the same way as for liquids. Independent of the sample preparation, either loose powder or pellet, the matrix of the sample is detected by the Compton Method. The selection of the sample preparation depends on the desired precision. For light elements like Na-S, pellets will give the most precise results.

4.1.2

The high dynamic range from the ppm up to % level is significant.

Figure 17 shows the calibration curve for Pb. The high dynamic range from the ppm up to % level is significant. The small RMS-value proves the performance of the matrix correction. The TURBOQUANT calibrations are based on 120 standard samples which are either pure chemicals like NaCl, CoO or PbO or certified reference materials from BCR (Brussels), Zentrales Geologisches Institut (Berlin), State Bureau of Metrology (China), Canadian Certified Reference Materials (Canada), National Bureau of Standards (USA), and the South African Committee for Certified Reference Materials (South Africa). The matrix correction is able to handle matrices starting from a 'light' matrix like wax (Hoechst) up to PbO, which represents the 'heaviest' matrix.

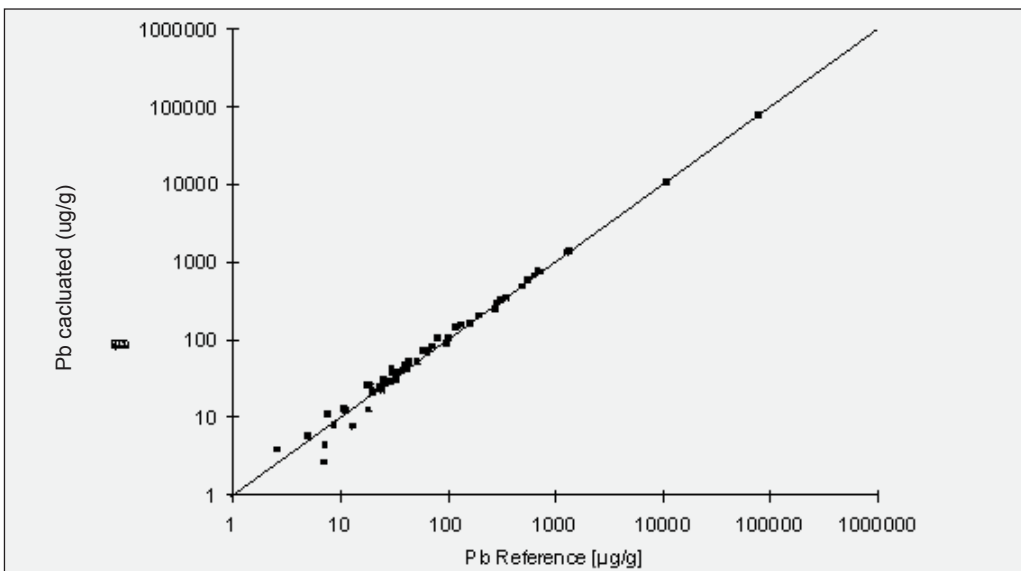


Figure 17: Calibration of Pb in pellets, 59 standards, RMS² = 0.006%, R=0.9999.

Tables 6-9 show the results using TURBOQUANT for different kinds of solid materials. NIST-1577 represents a 'light' matrix whereas BCR-176 represents a 'heavy' matrix.

Element	SPECTRO X-LAB 2000 Conc. [$\mu\text{g/g}$]	Certified Conc. [$\mu\text{g/g}$]
Na	1000 \pm 500	2420 \pm 60
Mg	<1000	601 \pm 28
P	10750 \pm 100	11000 \pm 300
S	7661 \pm 64	7850 \pm 60
Cl	2739 \pm 50	2780 \pm 60
K	9790 \pm 200	9940 \pm 20
Ca	123 \pm 46	116 \pm 4
Mn	< 12	10.5 \pm 1.7
Fe	189 \pm 17	184 \pm 15
Cu	167 \pm 11	160 \pm 8
Se	< 1.0	0.7 \pm 0.06
Br	10.7 \pm 1.2	(9.7)
Rb	12.7 \pm 1.2	13.7 \pm 1.1
Sr	< 1.0	0.1 \pm 0.001
Mo	3.2 \pm 1.4	3.5 \pm 0.3
Cd	< 1.0	0.5 \pm 0.03
Pb	< 2.6	0.1 \pm 0.004

Table 6:
Results using TURBOQUANT for a 'light' matrix: reference material NIST-1577b (bovine liver) prepared as pellet, total measurement time 150 s.

Element	SPECTRO X-LAB 2000 Conc. [$\mu\text{g/g}$]	Known Conc. [$\mu\text{g/g}$]
Br	9.5	10.0
Br	51	50.0
Br	97	100.0

Table 7:
Results using TURBOQUANT for the analysis of Br in polystyrene, prepared as loose powder, particle size 0.5 mm, total measurement time 150 s.

Element	SPECTRO X-LAB 2000 Conc. [%]	Certified Conc. [%]
Al	<0.02	(0.004)
Si	0.63 \pm 0.02	0.7
P	0.04 \pm 0.007	0.028
S	<0.01	0.0022
V	0.15 \pm 0.02	0.08
Cr	17.6 \pm 0.2	16.86
Mn	1.42 \pm 0.08	1.39
Fe	65.5 \pm 0.5	(64.81)
Co	0.4 \pm 0.08	0.4
Ni	12.9 \pm 0.16	13.15
Cu	0.25 \pm 0.02	0.29
Nb	0.027 \pm 0.006	(0.025)
Mo	2.00 \pm 0.04	2.2
W	0.058 \pm 0.005	0.05

¹ Value in brackets are not certified.

Table 8:
Results using TURBOQUANT for an alloy: stainless steel, 316, BS 84h, total measurement time 150 s.

Table 9:
Comparison of
results using
TURBOQUANT for
BCR-176 (ash)
prepared as
loose powder or
pellet. Total
measurement
time is 150 s.

Element	SPECTRO X-LAB 2000 Loose powder Conc. ¹		SPECTRO X-LAB 2000 Pellet Conc. ¹		Certified ²	Unit Conc.
Na	-		3.3	± 0.5	(4.3)	%
Mg	-		2.2	± 0.16	(2.18)	%
Al	-		9.13	± 0.12	(10.15)	%
Si	14.06	± 0.4	13.97	± 0.12	14.04	%
P	0.34	± 0.04	0.51	± 0.018	(0.55)	%
S	4.16	± 0.06	4.44	± 0.02	(4.46)	%
Cl	5.37	± 0.08	5.0	± 0.02	(4.8)	%
Cr	0.084	± 0.016	0.0085	± 0.012	0.086 ± 0.003	%
Fe	2.00	± 0.05	2.15	± 0.04	2.13 ± 0.11	%
Ni	134	± 22	125	± 22	123.5 ± 4.2	μg / g
Cu	1299	± 50	1232	± 54	1302 ± 26	μg / g
Zn	2.47	± 0.02	2.64	± 0.02	2.58 ± 0.04	%
Se	41.2	± 12	45	± 11	41.2 ± 2.1	μg / g
Cd	510	± 15	472	± 15	470 ± 9	μg / g
Sb	421	± 11	437	± 12	412 ± 18	μg / g
Hg	21	± 5	33	± 6	31.4 ± 1.1	μg / g
Pb	1.06	± 0.015	1.066	± 0.014	1.087 ± 0.017	%

¹ stat. Error (1σ). ² Value in brackets are not certified

In table 9, the results of BCR-176 are compared with two different sample preparation techniques. The comparison shows that for the analysis of the heavy elements (Z > 22) the preparation as loose powder is sufficient.

General

The results for the different sample types show the excellent performance of TURBOQUANT. It is a useful tool for classification and identification of unknown samples. Analyzing samples on the basis of liquid or solid calibration gives a high degree of flexibility. No special calibrations adapted to the sample type are required. The precision achieved for the heavy elements is generally <10 % relative and <20 % for the light elements.

4.1.3

Standardless

Standardless programs are based on fundamental parameters and describe the fluorescence process theoretically. The only unknown is the instrument itself. Therefore, the instrument geometry has to be measured on at least one sample. Standard-less programs will only give accurate results (error 20-30 % relative) as long as the matrix is known.

The major advantage of the TURBOQUANT method compared with these classic standardless methods is its matrix independence.

4.2

One of the biggest advantages of the theoretical methods is that they don't need standards to calibrate the inter-elemental effects.

4.3 Empirical / Lucas-Tooth & Price

The classical way to calibrate is to use standards with the same matrix and known composition. The measured intensities are then used to create a calibration curve (intensity vs. concentration). In XRF this is called an empirical calibration. The biggest difference between the theoretical method (fundamental parameters FP) and the empirical method is found in the use of inter-elemental corrections. Empirical methods do not correct for any of these effects. However, if the Lucas/Tooth method is used, corrections for inter-elemental effects can be introduced into the calibration. This is only possible as long as standards with and without these components are available. One of the biggest advantages of the theoretical methods is that they don't need standards to calibrate the inter-elemental effects.

Empirical methods are used to calibrate only a few elements in a fixed matrix, which will show a better degree of accuracy than theoretical methods.

Application Guide

5

Additives in Oil/Lubricants

5.1.1

Application:	Check of the elements Na-Zn in oil
Sample Prep:	Pouring liquid into sample cup
Precision:	1-3 %
LOD:	> 100 ppm
Quantification:	Fundamental Parameters, empirical
Test method:	ASTM D6481-99

Used oil

5.1.2

Application:	check of wear metals
Sample Prep:	Homogenize the used oil, pour it into a sample cup
Precision:	10-20 %
LOD:	~ 1-10 mg/kg
Quantification:	Fundamental Parameters, empirical

Wear Metals/Cooling Liquids

5.1.3

Application:	Check of additive elements Na-Zn and wear metals in oil/emulsions
Sample Prep:	Pouring liquid into sample cup
Precision:	10 %
LOD:	> 1 ppm
Quantification:	Fundamental parameters with automatic matrix correction (e.g.,TURBOQUANT)

Fuels

5.1.4

Application:	Check of S
Sample Prep:	Pouring liquid into sample cup
Precision:	1-3 %
LOD:	~1 ppm
Quantification:	Fundamental Parameters, empirical
Test methods:	ASTM 6445-99, ASTM 4294-90, EN ISO 20847, IP 496, draft norm ASTM WK 7530/EI polarization EDXRF

Waste

5.1.5

Application:	Screening of all elements between Na and U
Sample Prep:	Pellets, powders and liquids in sample cups
Precision:	10-20 %
LOD:	>0.5 ppm
Quantification:	Fundamental parameters with automatic matrix correction (e.g.,TURBOQUANT)
Test methods:	ASTM D5839-96, ASTM D6552-97, draft norm CEN TC 292 WG3

5.1.6 RoHS, WEEE, ELV

Application:	Analysis of Cr(VI), Cd, Pb, Hg, PBB, PBDE, XRF only determine the overall content of Cr and Br
Sample Prep:	direct, powder, granulates
LOD:	~ 5 mg/kg
Quantification:	Fundamental parameters with automatic matrix correction (e.g.,TURBOQUANT), empirical
Test methods:	IEC draft norm

5.1.7 Polymers

Application:	Analysis of flame retardant elements containing Br and Sb
Sample Prep:	pressed pellets, direct, powder, granulates
LOD:	~ 5 mg/kg
Quantification:	Fundamental parameters with automatic matrix correction (e.g.,TURBOQUANT), empirical
Application:	Analysis of additive elements
Sample Prep:	pressed pellets, direct, powder, granulates
Quantification:	Fundamental parameters with automatic matrix correction (e.g.,TURBOQUANT), empirical

5.1.8 Minerals/Geology/Ceramics

Application:	Check of main components
Sample Prep:	Fused beads
Precision:	0.2 %
LOD:	> 100 ppm
Quantification:	Fundamental parameters or alpha coefficients
Test methods:	DIN 51001
Application:	Check of trace elements
Sample Prep:	Pellets
Precision:	1-10 %
LOD:	>0.2 ppm
Quantification:	Fundamental parameters or empirical method

5.1.9 Cement

Application:	Check of main components
Sample Prep:	Fused beads or pressed pellets
Precision:	0.2 %
LOD:	> 100 ppm
Quantification:	empirical
Test methods:	ASTM C114, ISO DIS 680

Metals		5.1.10
Application:	Screening of metals	
Sample Prep:	Polishing surface	
Precision:	10-20 %	
LOD:	> 100 ppm	
Quantification:	Fundamental parameters with automatic matrix correction (e.g.,TURBOQUANT)	
Precious metals		5.1.11
Application:	Quantification of alloying elements	
Sample Prep:	Polishing surface	
Precision:	~ 0.1 %	
LOD:	>0.01 %	
Quantification:	Fundamental parameters	
Iron ore and Sinter		5.1.12
Application:	Check of main components	
Sample Prep:	Fused beads	
Precision:	1-3 %	
Quantification:	empirical	
Slag		5.1.13
Application:	Check of main components	
Sample Prep:	Fused beads, pressed pellets or powders in cups	
Quantification:	empirical	
Test methods:	DIN 51001	
Ferroalloys		5.1.14
Application:	Check of main components	
Sample Prep:	Pellets	
Precision:	1-3 %	
LOD:	> 100 ppm	
Quantification:	Empiric calibration	
Remark:	Ferroalloys show big particle size effects. Therefore, standards must represent the same grain size effects as the samples do. No international standards can be used for calibration.	
Pharmaceutical		5.1.15
Application:	Check of trace elements	
Sample Prep:	Pellets, powder in a sample cup	
Precision:	1-10 %	
LOD:	>0.2 ppm	
Quantification:	Fundamental parameters with automatic matrix correction (e.g.,TURBOQUANT for pharmaceuticals)	

5.1.16 Food

Application:	Na, Mg, P, Cl, K, Ca, Fe, Zn in milk powder
Sample Prep:	Pellets, powders in sample cups
Precision:	1-5 %
LOD:	>0.5 ppm
Quantification:	Fundamental parameters or empirical methods

Appendix

6

Literature

6.1

Basics

6.1.1

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6.1.6 Applications

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6.2 Figures

- Figure 1: Penetration depth of x-rays for light elements. To get reproducible results, you need a grain size of $0.02 \mu\text{m}$. This is not achievable!
- Figure 2: Measurement of fluorine. Absorbance of fluorine intensity by films covering the bottom of a sample cup. Main reason why fluorine cannot be measured in sample cups.
- Figure 3: Exciting x-rays are absorbed by the matrix until they reach the element to excite. The fluorescence radiation (here Zn) is absorbed until it leaves the sample by the matrix. In this example, the matrix is an organic solvent. If the matrix changes (e.g., to water) also the absorption of x-rays will change.
- Figure 4: Each solvent shows a different absorption of x-rays. The Mo radiation from the Mo secondary target used for excitation is scattered at the sample. Also the scattering shows a matrix dependence. This can be used for matrix correction (e.g., in TURBOQUANT).
- Figure 5: Comparison of resolution of different types of detectors used in EDXRF.
- Figure 6: Comparison of peak to background ratios of different types of Si(Li) detectors used in EDXRF.
- Figure 7: Cartesian geometry for polarization of exciting x-rays.

- Figure 8: Comparison of spectra of certified reference material (BCR-186) with direct excitation (1) and polarized radiation (2).
- Figure 9¹: Mill with a ZrO₂ grinding vessel for grinding of up to 10 g.
- Figure 10²: Mill with a Al₂O₃ grinding vessel for grinding of up to 60 g.
- Figure 11¹: Manual press up to 15 tons.
- Figure 12¹: Example for different types of dies.
- Figure 13¹: Fusion Machine (2 burners, also available with 4 burners).
- Figure 14: Excitation of K and L lines with different targets.
- Figure 15: Influence of different matrices to the intensity of chlorine K α -line. Measurement was done by an HOPG-target, 10 kV, 200 s.
- Figure 16: Calibration of halogens in liquids by TURBOQUANT. Measurement time 200 s.
- Figure 17: Calibration of Pb in pellets, 59 standards, RMS = 0.006 %, R=0.9999.

¹ Figure 9, 11, 12 and 13: With friendly permission by Fluxana, Accessories & Application Support for X-Ray Fluorescence Analysis

² Figure 10: With friendly permission by Breitländer

6.3

Tables

- Table 1: Overview of elements detectable with XRF.
- Table 2: Targets and corresponding elements in TURBOQUANT.
- Table 3: Results of TURBOQUANT liquid for Cl in different solvents.
- Table 4: Results of a polyphased sample, total measurement time 600 s, 3 g sample + 1 g charcoal as absorbing material.
- Table 5: Reproducibility of an ICP multi-element standard prepared 3 times with charcoal (3 g sample + 1 g charcoal).
- Table 6: Results using TURBOQUANT for a 'light' matrix: reference material NIST-1577b (bovine liver) prepared as pellet, total measurement time 150 s.
- Table 7: Results using TURBOQUANT for the analysis of Br in polystyrene, prepared as loose powder, particle size 0.5 mm, total measurement time 150 s.

Table 8: Results using TURBOQUANT for an alloy: stainless steel, 316, BS 84h, total measurement time 150 s.

Table 9: Comparison of results by TURBOQUANT of BCR-176 (ash) prepared as loose powder or pellet. Total measurement time is 150 s.



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