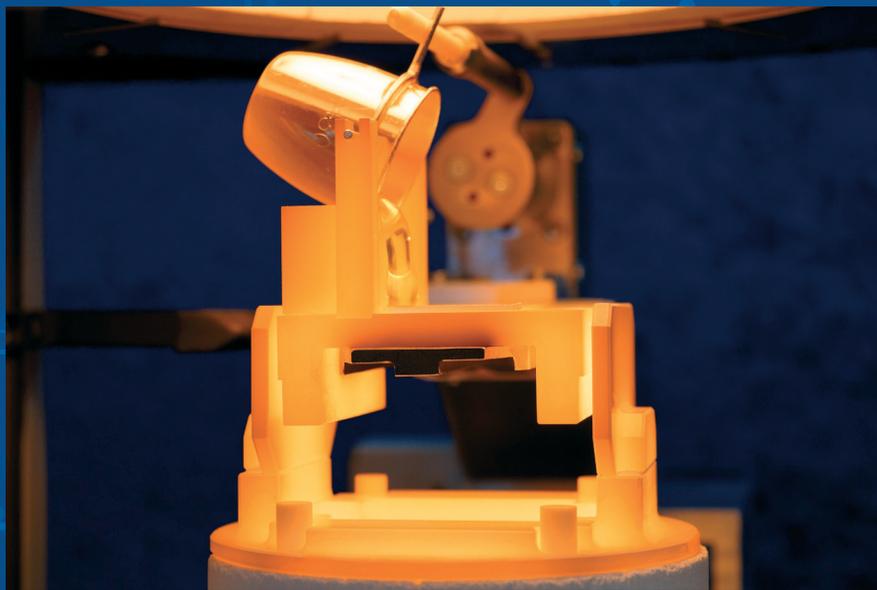


X-Ray Fluorescence Analysis: Practical and Easy

2nd edition

Rainer Schramm



FLUXANA[®]
XRF Application Solutions

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Dear XRF user,

The first edition of this book, in German and English from 2012, was a great success and it was sold out within three years. This has motivated me to adapt the content to the latest state of technology and to publish a second expanded edition.

Various information and criticism from the readers has also been taken into consideration. Great care was taken especially when amending statistical parameters, such as the definitions for precision, accuracy and measurement uncertainty.

Fusion with an electric furnace is now discussed in the sample preparation section. Especially the latest developments concerning the analysis of volatile elements have been taken into account.

Since its launch over a decade ago, FLUXANA has provided XRF users with sample preparation instruments, consumable materials, application know-how and regular training courses. To date, more than 1000 users worldwide utilize our fusion systems and proven application packages. This book is dedicated to all existing and future users of XRF and is intended to provide a deeper insight into the practical daily use of XRF with special focus on sample preparation, as this can be one of the biggest sources of error found with the technique.

The reader will find that XRF theory is not too heavily detailed here, but references to tried and tested textbooks on XRF theory are given in suitable locations. In fact, the practical application of the technique is more the book's focus. Basic terms are explained, and details of the many different types of XRF instruments that are available are tabulated. Sample preparation techniques are shown in easy to follow picture steps and many real-life application problems are shown together with proven tips on their solution.

Fluxana always welcomes new XRF challenges. Any user not finding a suitable solution to their application problem in the pages of this book is encouraged to contact the Fluxana team at www.fluxana.com.

1 X-Ray Fluorescence Analysis (XRF)

1.1 Origins

X-ray fluorescence radiation is an electromagnetic radiation with high energy (Fig. 1). Energetically it lies between γ radiation and UV radiation.

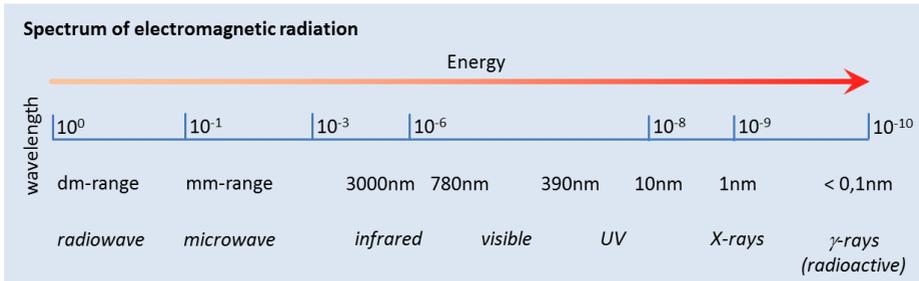


Fig. 1 Spectrum of electromagnetic radiation [1].

X-ray fluorescence is generated by, among other processes, the ionization of the inner shell of an atom. However, the probability that it will occur is small and is also dependent on the atomic number of the atom. Most of the excitation energy is translated into heat, which is the reason that XRF instruments always need to be more or less cooled.

If ionization of an inner shell does occur, i.e., an electron is removed, then the hole is filled by an electron from a higher energy shell. The energy difference is released as X-ray fluorescence radiation and is characteristic for the element. Depending on which transition takes place, it is called K, L or M radiation.

Fig. 2 shows the typical electron transitions for the different shells. The lower line represents the innermost shell of an atom. The arrows symbolize an electron transition that is accompanied by the formation of an X-ray fluorescence line, such as, e.g., $K\alpha_1$. The intensity of the lines decreases in the order $K\alpha$, $K\beta$, $L\alpha$, $L\beta$.

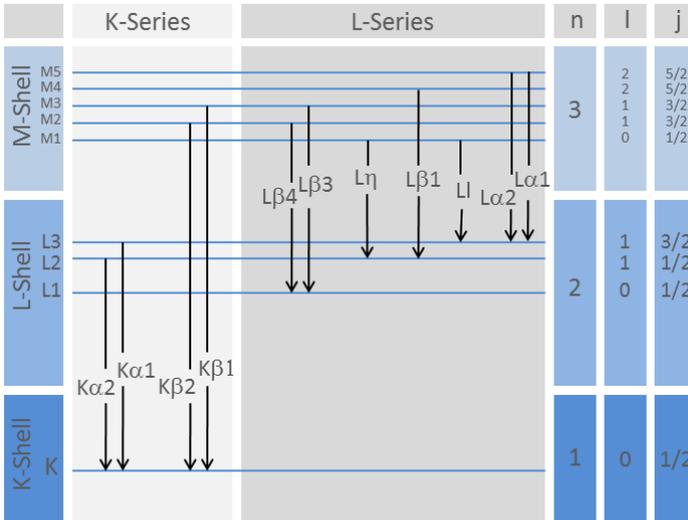


Fig. 2 Transition of electrons in inner shells [2].

1.2 Element Range

Accordingly, every observed element can be assigned a characteristic pattern of X-ray fluorescence radiation lines. The energy of the element-dependent radiation increases with increasing atomic number. Thus, the penetration of material also grows. On the other hand, radiation from elements with a low atomic number is easily completely absorbed by other materials. In practice, this means that fluorine is the element with the smallest atomic number that can be analyzed with today's typical XRF instrument, although theoretically and practically (with a great deal of effort) the analysis of beryllium is also possible. Uranium is usually given as the element with the highest atomic number. Most of the elements with higher atomic numbers are radioactive, and as such, of less importance in practice.

This means that from fluorine to uranium, 72 elements can be analyzed with XRF; almost the periodic table of elements, which is the reason for the widespread use of this technique.

1.3 Instrument Technology

Depending on the method of detection, instrument technology is divided into energy dispersive (EDXRF) and wavelength dispersive (WDXRF) X-ray fluorescence analysis.

1.3.1 Energy Dispersive X-Ray Fluorescence Analysis (EDXRF)

With EDXRF, the sample is excited by the X-ray tube directly or through a filter (Fig. 3). A semiconductor detector (e.g., silicon-lithium semiconductor, pin diode or silicon drift chamber) analyzes the X-ray fluorescence radiation that comes directly from the sample.

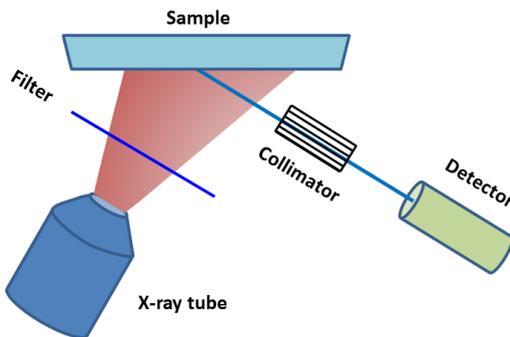


Fig. 3 Energy dispersive X-ray fluorescence (EDXRF) with direct excitation.

Here, the detector together with the associated electronics counts and sorts, according to energy, all of the photons that reach it. A pulse height spectrum that indicates the number of photons or impulses for a given energy is established. The detector typically has only a few μs for processing, so that processing is accordingly limited to approximately 1,000,000 pulses per second. Using a filter, a portion of the exciting radiation can be screened out to avoid overloading the detector.

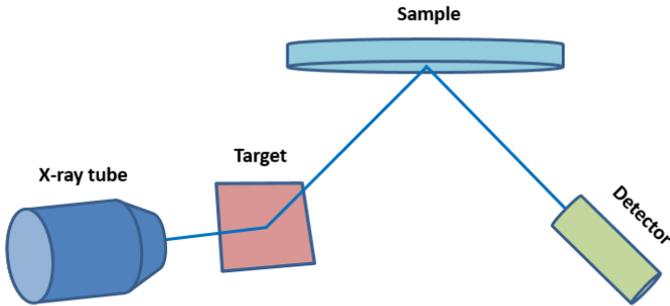


Fig. 4 Energy dispersive X-ray fluorescence (EDXRF) with polarized excitation.

XRF with polarizing excitation represents a further possibility for EDXRF (Fig. 4). Here, the radiation coming from the tube is deflected by 90° and is then used to irradiate the sample. The detector must be perpendicular to the plane determined by the tube, target and sample. The most important effect is that by deflecting the X-ray radiation by 90° , the radiation is polarized and the spectral background in the spectrum is reduced.

1.3.2 Wavelength Dispersive X-Ray Analysis (WDXRF)

WDXRF uses, like some EDXRF, direct excitation (Fig. 5). Here it is also possible to work with filters to block or weaken components of the excitation radiation. The major difference is the method of detection of the X-ray fluorescence radiation for WDXRF. Using a goniometer, only one wavelength from the spectrum is fed to the detector, i.e., it measures only one line from one element. In order to conduct multiple element analyses, it is necessary to create a serial measuring program that drives to and analyzes all of the lines of interest; one after another. There are, however so-called simultaneous spectrometers: In this case, there is a set channel for each element consisting of a fixed crystal with corresponding detector arranged around the sample. When combined with a goniometer this forms a very fast, high performance XRF instrument that is especially useful for process control.

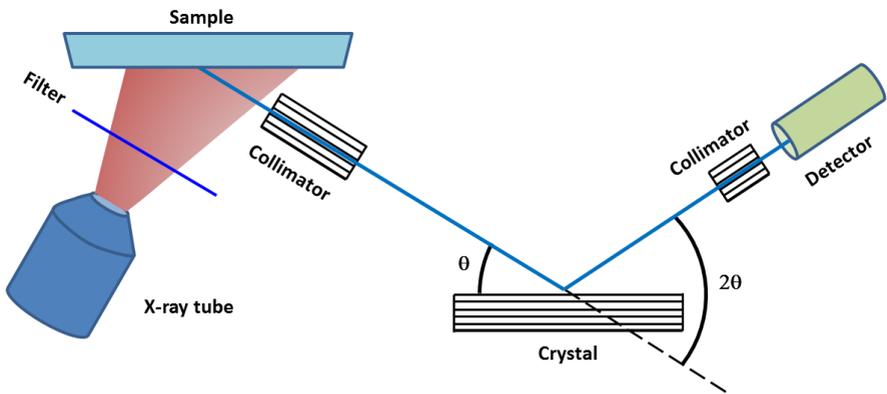


Fig. 5 Wavelength dispersive X-ray fluorescence (WDXRF).

1.3.3 Comparison: EDXRF - WDXRF

In general, it is possible to say that the two techniques are complimentary; one supplements the other. EDXRF has a time advantage, as all elements are measured simultaneously, whereas the (serial) WDXRF measures the elements one after another.

WDXRF has a resolution and sensitivity advantage which is especially useful in the range of atomic numbers up to 30 and 55 to 80.

The differences become less distinct for the larger atomic numbers. The differences in the energies between the lines continue to become larger, thus the resolution advantage for WDXRF decreases. At the same time, the yield on fluorescence increases and with it, the sensitivity of the elements, so that in end effect, EDXRF achieves better detection limits than WDXRF.

1.3.4 Additional XRF Instruments

As the X-ray tubes became smaller, it became possible to construct very small portable X-ray fluorescence instruments (Fig. 6). These usually have the form of a pistol, with which a given material can be directly analyzed onsite. Although the measurement has become very simple in this way, it is important not to neglect the aspects of sample preparation.

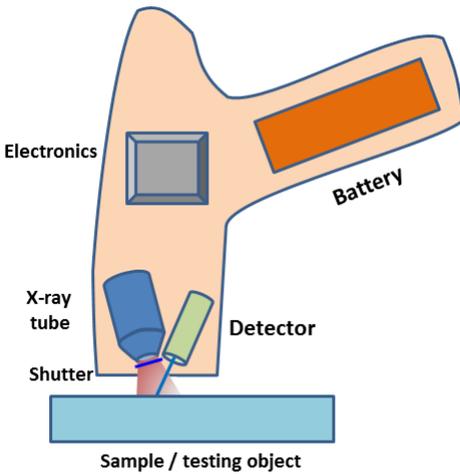


Fig. 6 Portable XRF instrument based on EDXRF.

So-called micro XRF instruments use a focusing X-ray beam to excite the sample. The diameter of the beam is typically between 1 mm and 30 μm ; making spatially resolved XRF possible. The sample is first recorded optically. The location for the analysis is then determined on the photo. This procedure is known as “spotting” (Fig. 7).

The step-by-step analysis of a given surface of the sample is another possibility. This is called “mapping”. In a 3D representation, Fig. 8 shows the intensity measured for four different elements along the z-axis and the corresponding measuring points in the x/y plane of the sample surface. Spatially resolved information, e.g., about inclusions or material defects can also be obtained with this technique.

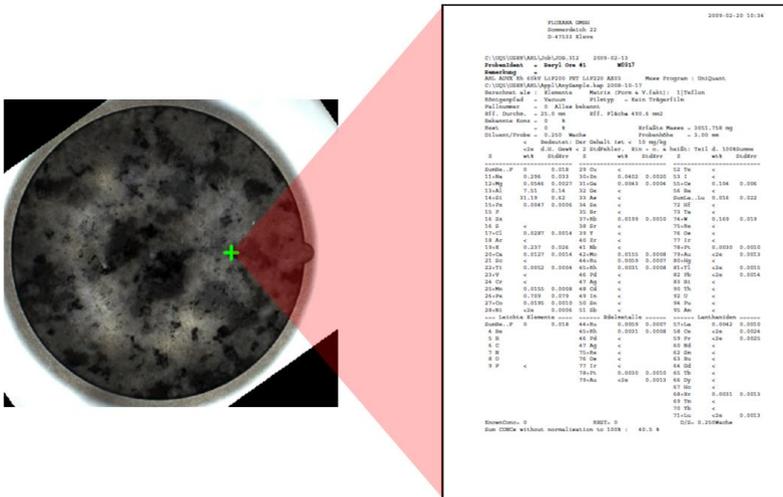


Fig. 7 Spotting with micro xrf instrument to analyse a dedicated point on the sample.

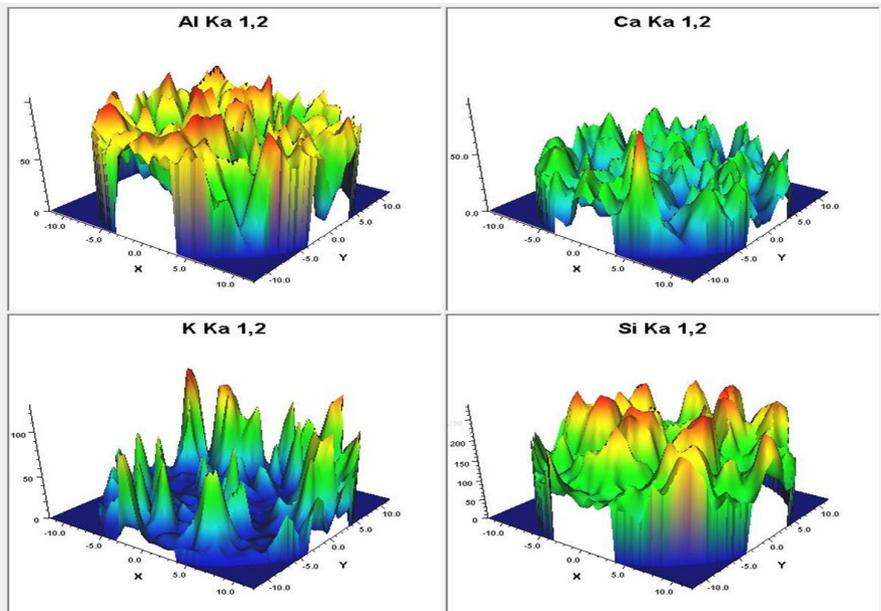


Fig. 8 Area mapping of Al, Ca, K, Si in Granite.

1.3.5 Radiation Protection

Most XRF instruments in our laboratories meet the requirements for full-protection instruments according to the German X-ray protection ordinance. This means that an effective dosage of 7.5 $\mu\text{Sv/h}$ at a distance of 10 cm from all contact surfaces is allowed. If a type-approved instrument is concerned, operation must be reported to the appropriate authority (a radiation protection officer is not required). If the instrument is not type-approved, then operation must be authorized by the appropriate authority and a radiation protection officer is necessary [3].

1.4 Application Development of a Test Method

Utilization of XRF can only be successful if it is integrated into a complete testing method. The following steps are necessary in order for such a method to work:

- Definition of the analytical performance
- Definition of the elements and the concentration ranges
- Selection of the sample preparation
- Selection of the standard samples
- Determination of the measuring conditions
- Calibration
- Validation

Performance of these steps ensures that the test method is robust and reliable and that testing with certified reference materials takes place.

The basic German XRF standard, DIN 51418-2 [4], can be considered as an example of a test method. It will also soon be available in English.

1.4.1 Definition of the Analytical Performance

In order to define the analytical performance, I would like to refer to statistical parameters as defined in, e.g., NORDTEST [5] or the ISO standard method 29581-2 [6].

1.4.1.1 Repeatability

Repeatability is understood to be the standard deviation of an element concentration that is determined with the same test method on an identical sample in the same laboratory by the same user with the same XRF instrument within a short amount of time.

If a single sample, e.g., prepared as a pellet, is measured ten times, then the repeatability of an instrument is obtained.

This error should be determined with a typical sample. It should be smaller than the sample preparation error and corresponds to the measuring error for the XRF instrument (see chapter 1.4.1.5).

If a single sample, e.g., prepared as a pellet, is newly prepared ten times and then measured, then the repeatability of the sample preparation and the XRF instrument is obtained.

Since the sample preparation error is generally significantly greater than the measuring error, its repeatability indicates the quality of the sample preparation method.

1.4.1.2 Reproducibility

Reproducibility is understood to be the standard deviation of an element concentration that is determined with the same analytical principle but under

modified conditions, e.g., in different laboratories by different users with different XRF instruments.

This is typically the case for proficiency tests, where a sample that is as identical and homogeneous as possible is sent to different laboratories and analyzed with a stipulated testing method.

If the standard deviation of an element concentration of the same, repeatedly newly prepared sample is determined over a year in the same laboratory, then it is known as within-laboratory reproducibility.

1.4.1.3 Trueness

The trueness compares the concentrations determined with the test method with the certified values of a certified reference material. The difference is also referred to as “bias.”

This works best for methods based on a constant matrix. The trueness can be checked with a few certified or known control samples. This is more complicated for procedures that encompass different matrices. In this case, a concentration-dependent function is applied to calculate the trueness (see e.g., ISO 12677 [7]) or the respective control samples should be kept available for different concentration and matrix ranges.

1.4.1.4 Accuracy or Measurement Uncertainty

Accuracy is the combination of repeatability and trueness.

Measurement uncertainty is an estimation of the analytical error for an analysis assuming a certain probability of error based on random errors (repeatability) and systematic errors (trueness).

Figure 9 is an overview of the terms and their connections.

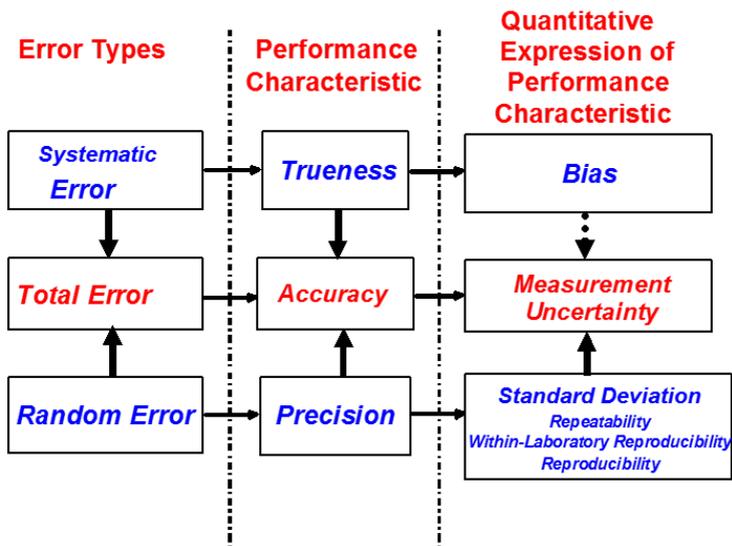


Fig. 9 Overview and interrelation of the terms that contribute to the measurement uncertainty [8].

1.4.1.5 Measurement Error

The measurement error in XRF is directly determined from the intensity measured for a line. The rules for counting statistics are valid since the detection process deals with counting pulses (counts). Formula (1) shows the calculation of the absolute error from the pulses measured during the entire measurement time. It is clear that the number of pulses is directly dependent on the measurement time. Please note that the intensity of a line is usually given as a number or pulse rate in counts per second. For this reason, it is necessary to first multiply by the measuring time in order to calculate the absolute counting error.

$$s = \sqrt{N} \quad (1)$$

- s Statistical measurement error
 N Sum counts within total measurement time

Table 1 shows the relative measurement error depending on the measuring time. In practice, the smallest possible relative error for an XRF measurement lies in the range of $< 0.05\%$. In order for the measurement error to be negligibly small in a testing method, the measurement time for the main components should be chosen so that approximately one million pulses are achieved. It is normally not possible to achieve this type of pulse rate for trace components. The data in Table 1 can be used to determine a practical measuring time; one for which the corresponding measuring error meets the requirements for the testing method.

Table 1 shows the relative measurement error of a fluorescence line with e.g. 1000 counts per second depending on the measurement time.

Count rate [counts*s ⁻¹]	Meas. Time [s]	Sum Counts N	Rel. Meas. Error s
1.000	1000	1.000.000	0,1%
1.000	100	100.000	0,3%
1.000	10	10.000	1%
1.000	1	1.000	3%

1.4.1.6 Standard Methods

The easiest possibility for defining the performance data for a testing method is when a standard method already provides for it. A number of standard methods have already been determined for XRF. Table 2 offers an overview of the standards that stipulate XRF as the analytical technique. The list is by no means complete.

Here I would like to provide a brief overview of the various standard method systems: ISO standards are valid worldwide; EN standards in Europe and DIN standards in Germany. Other national standards include, e.g., ASTM for USA; IP for Great Britain, NF for France, etc.

An attempt to harmonize the standard methods has been made, so that, e.g., DIN EN ISO 20884 is a standard method recognized and implemented in all three regions: DIN, EN and ISO.

Table 2 shows standard methods describing xrf as the analytical technique.

Standard	Purpose
DIN 51418-2	Terms and basic information for measurement, calibration and evaluation
DIN 51729-10	Analysis of ash with XRF
ASTM D4326 – 04	Analysis of ash with XRF
EN ISO 12677	Analysis of refractories with XRF
DIN 51001 Beiblatt 1	Analysis of oxidic raw materials with XRF
ISO 9516-1	Analysis of iron ores with XRF
EN 15309	Analysis of waste and soil with XRF
ISO 29581-2	Analysis of cement with XRF
DIN EN ISO 20884	Analysis of S in fuels with WDXRF
DIN ISO 15597	Analysis of Cl, Br in petroleum products with WDXRF
DIN EN ISO 13032	Analysis of S in fuels with EDXRF
DIN 51399-2	Analysis of additives and wear metals in lubricants with WDXRF
ASTM D 2622 – 98	Analysis of S in petroleum products with WDXRF

1.4.2 Definition of the Elements and Concentration Ranges

Each time a new application is created, it is necessary to decide which elements are to be determined. Above all, it is important to consider the concentration ranges in which this is to take place. Further conclusions can be made from these considerations:

- Selection of the sample preparation
- Selection of the standard samples
- Determination of the measuring conditions

1.4.2.1 Selection of the Sample Preparation

It can be seen in Table 3 that the sample preparation method determines the analytical error, i.e., the repeatability. In order to achieve the performance