

**Announcing the publication
of a unique new XRF book**

Guidelines for XRF Analysis

**Setting up programmes for
WDXRF and EDXRF**



James Willis

Clive Feather

Ken Turner

Website: www.xrfguidelines.co.za

Guidelines for XRF Analysis contains everything you've ever wanted to know about setting up successful XRF analytical programmes. This book is loaded with detailed analytical guidelines for geological materials, commodities and industrial materials that are suited to analysis by XRF.

It is a one stop XRF reference manual, and no XRF laboratory should be without it. Sample preparation describes well-tried and tested methods, and there is sufficient theory to enable the reader to gain maximum advantage from the book. Trace elements, grouped by spectral region, are carefully evaluated, and the authors, with a combined XRF experience of over 130 man years, share with you their accumulated knowledge, "tricks-of-the-trade", and information on

- Optimum settings for WDXRF and EDXRF instrumentation
- The most suitable analyte spectral lines
- The best background positions to measure
- Identification and correction of line overlap, and
- Choice of procedures for matrix correction

Determine with confidence fluorine to uranium, atomic number 9 to 92, in a wide range of materials.

If you are working on any of the following commodities or materials, you need this book. Commodities and materials chapters are self-contained and have all the information needed to analyse:

- Silicate rocks
- Exploration samples
- Alloys of precious metals
- Activated carbon and catalysts
- Ferrochrome & Ferromanganese
- Lateritic nickel ores
- Iron ores and slags
- Aluminium ores and alumina
- Mineral sands & heavy minerals
- Refractories and ceramics
- Plastics and polymers
- Fuels, oils and wear metals
- Metal alloys
- Coal and coke
- Environmental materials
- Sulphide base metal ores
- Uranium ores and "Yellow cake"
- Cements and carbonates

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Guidelines for XRF Analysis – Setting up Programmes for WDXRF and EDXRF

By James Willis, Clive Feather and Ken Turner

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544 Pages, 253 Figures in full colour, 138 Tables

Example taken from the chapter on Wavelength Dispersive XRF

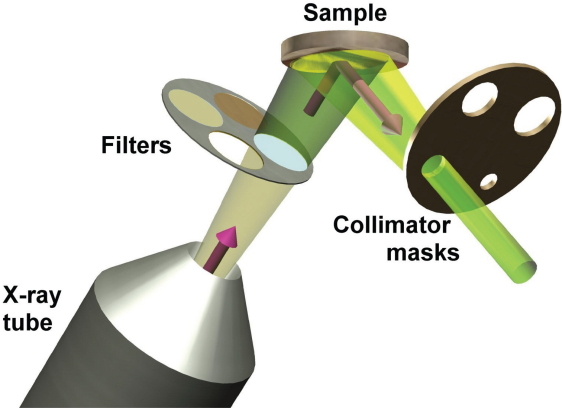


Figure 4-10. The location of primary beam filters and collimator masks in a WDXRF spectrometer. Collimator masks, with different apertures that match sample cup apertures, are located between the sample and the primary collimator. They are used to ensure that only radiation from the sample reaches the collimator.

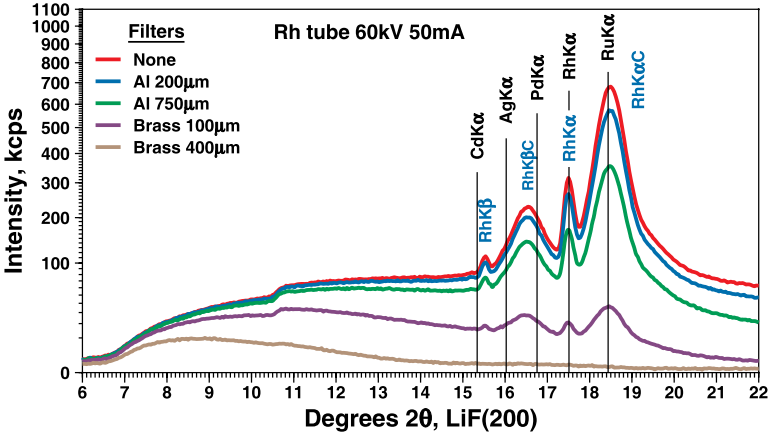


Figure 4-11. The removal using primary beam filters of Rh tube K lines interfering in the determination of Cd, Ag, Pd, Rh and Ru.

for these elements the FOM values are the same or better with or without a primary beam filter.

For elements such as Mo, Nb, Zr, Y, Sr and Rb the use of a “thick” or “thin” brass filter is counter productive. Although they reduce the background considerably, they also filter out all or most of the Rh K lines which are the prime exciting wavelengths of the K lines of elements Mo to Rb and the L lines of elements U to Pb.

Example of a page of the book showing WDXRF and EDXRF spectral scans, analyte peaks, background positions and potential line overlaps.

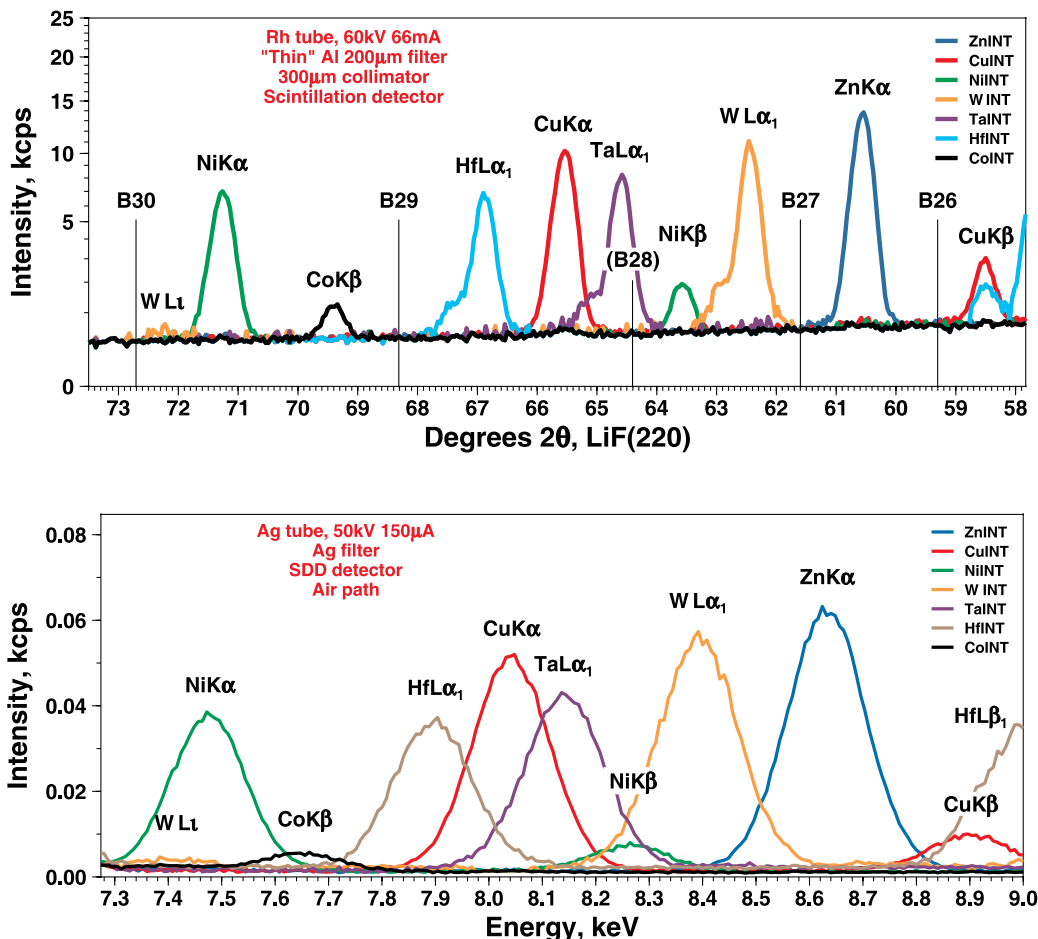


Figure 11-7. WDXRF (Top) and EDXRF (Bottom) spectra over Zn, Cu and Ni K lines and W, Ta and Hf L lines; 1000 ppm for K lines and 2000 ppm for L lines.

Select the counting time for each set of analysis conditions such that measurements will yield the required precision (counting errors) and LLDs (see Chapter 4, Section 4.3.12).

11.3 ADDITIONAL COMMENTS

A common problem with this group of elements is the presence of impurities in the tube target or tube housing, especially Cu and Ni. The result is small peaks of Cu and Ni in the tube spectrum that are scattered off the sample (Figure 11-8). The fact that the net intensities of the peaks are present in all blank samples, and in inverse proportion to the sample MAC, is a sure indication that the peaks are part of the tube spectrum and do not arise from Cu and Ni in the samples. The tube peaks are part of the background and their intensity must

Example of pages taken from Tables 32-4 and 32-5 in the Tables chapter.

Table 32-4 (cont). Recommended WDXRF instrumental parameters for the determination of major, minor and trace elements, and 2θ angles for peak and background positions for different analysing crystals.

Element	Line	Rh tube	Filter	Crystal	Collimator	Detector	Analysing crystal degrees 2θ		
		kV/mA					LiF(420)	LiF(220)	LiF(200)
B28		60/max	None/ "thin" Al	LiF(220)/ LiF(200)	Fine/ Medium	SC		64.4	44.3
Ta	$L\alpha_1$							64.61	44.42
Cu	$K\alpha$							65.56	45.03
Hf	$L\alpha_1$							66.89	45.88
B29								68.3	46.8
Lu	$L\alpha_1$							69.31	47.43
Co	$K\beta$							69.38	47.47
Ni	$K\alpha$							71.27	48.67
Yb	$L\alpha_1$							71.90	49.06
B30								72.7	49.6
Dy	$L\beta_1$							73.83	50.28
Tm	$L\alpha_1$							74.65	50.79
Fe	$K\beta$		No filter		Fine		76.16	51.73	

Table 32-5 (cont.). Analyte elements, analyte lines and possible spectral overlaps.

Analyte element	Analyte line	Possible spectral overlaps
Ge	$K\alpha$	$W L\beta_2$, $Hg L\alpha_2$, $Ta L\beta_5$, $W L\beta_3$
Ga	$K\alpha$	$Ta L\beta_1$, $Ta L\beta_4$, $Hf L\beta_2$, $Hf L\beta_3$, $Pb L\alpha$
Zn	$K\alpha$	$Cu K\alpha$, $Cu K\beta$, $W L\alpha_{1,2}$, $Ta L\eta$
Cu	$K\alpha$	$Ta L\alpha_{1,2}$, $Ni K\beta$, $W L\alpha_{1,2}$, $Hf L\eta$
Ni	$K\alpha$	$W L\alpha$, $Zr K\alpha(2)$, $Co K\beta$
Co	$K\alpha$	$Fe K\beta$, $Er L\alpha_1$, $Hf L\alpha$, $Tb L\beta_1$, $Er L\alpha_2$, $Nd L\gamma_{3,2}$
Fe	$K\alpha$	$Mn K\beta$

Example taken from the chapter on Sample Preparation

2.3 CRITICAL (ANALYSIS) DEPTH

The analysis depth in the sample (as a powder pellet, fused bead, metal block, liquid, or the like) as presented to the spectrometer, also known as the critical depth or critical thickness, is the depth beyond which a given spectral line will not emerge from the sample (Figure 2-1). It is a function of the sample composition and associated mass attenuation coefficient (mass absorption coefficient or MAC; See Glossary for a definition of MAC, and Chapter 4, Section 4.3.2.1 for examples), sample density, the spectrometer geometry and the spectral energies of the primary and secondary X-rays. Samples that are thicker than the critical depth are said to be 'infinitely thick'.

The analysis depth can be calculated using the formula

$$d = \frac{4.61}{\mu\rho} \cdot \sin\psi_2$$

where

ψ_2 is the take-off (emergent) angle

μ is the sample mass attenuation coefficient at the spectral wavelength of interest

ρ is the sample density.

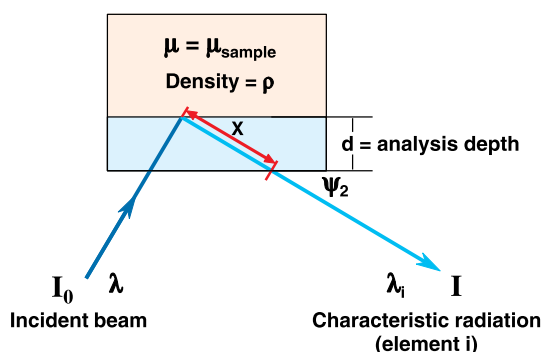


Figure 2-1. Analysis depth and the factors determining its magnitude.

From Willis et al (2011), courtesy of PANalytical B.V.

Examples of critical analysis depths for eight different wavelengths for twelve materials with very different densities and mass attenuation coefficients and a 40° take-off angle are given in Table 2-2. "Critical mass" is defined and calculated here as the mass of sample required to provide critical analysis depth in a 40mm diameter sample. It is more reliable for pressed powder pellets as it allows for porosity. Examples of "critical mass" for the same samples and same wavelengths as in Table 2-2 are given in Table 2-3.

Since analysis depth and critical mass are dependent not only on sample density and MAC but also on the take-off angle, conversion factors for different take-off angles relative to 40° are given in Table 2-4. They allow the analyst to calculate analysis depths and critical mass for the samples and wavelengths in Tables 2-2 and 2-3 for spectrometers with take-off angles other than 40° .

6.7 CALIBRATION STRATEGIES

6.7.1 Calibration strategies for fused beads

There are a number of calibration strategies that can be adopted for XRF major and minor element analysis. These are based on: a range of standards, preferably CRMs; synthetic single, binary and multi-element standards; and internal standards.

Background and spectral overlap corrections should be applied where appropriate, and matrix corrections should be carried out using theoretical influence coefficients (alpha factors) calculated from fundamental parameters, or by direct application of fundamental parameters.

Loss of CO₂ and other volatile components during fusion must be taken into account in the matrix correction procedure. Loss (LOI) may be measured and input into the matrix correction software, estimated by difference, or "loss eliminated alphas" may be used.

When estimated by difference,

Loss = 100 – (sum of all measured analytes expressed in their correct oxide form).

All elements present at more than trace levels must be determined, otherwise they will appear in the reported "Loss".

It is strongly recommended that empirical matrix corrections be avoided. The only exception being for pressed powder analysis, where it is sometimes possible to correct (to a limited extent) for particle size and mineralogical variations using empirical matrix corrections. Use with care and thoroughly test with suitable CRMs, and a few samples of known composition, over the full expected mineralogical and compositional range.

6.7.1.1 Calibration using CRMs and/or analysed samples

Fused beads are prepared from a set of CRMs and/or analysed samples covering the full expected elemental and compositional range including LOI. To improve the precision of the calibration and to aid in the identification of "bad" beads it is strongly recommended that the standards be prepared in duplicate or triplicate. Care must be taken to include elements that are required only for spectral interference correction as well as those to be reported.

This is arguably the most commonly used calibration strategy and is applicable to virtually all material types. Its main limitation is the availability of high quality standards that cover the required elemental and compositional range.

6.7.1.2 Calibration using a single multi-element synthetic standard ("Line only" method)

Example taken from the commodity chapter on Mineral Sands

18.2 MINERAL SANDS

18.2.1 Introduction

Modern and palaeo alluvial sands may contain concentrations of heavy minerals of which zircon, rutile, ilmenite, monazite, titanomagnetite, garnet and cassiterite are the most abundant. The minerals may be altered by weathering or by metamorphic activity in the host rocks from which they are derived. The heavy minerals are separated from the sands by several physical techniques exploiting specific gravity and magnetic and electrostatic susceptibility. XRFS is used to analyse exploration samples, plant feeds and a range of concentrates and intermediate plant products. At some locations, smelting is used to reduce ilmenite to pig iron and to a Ti-rich slag that may be analysed by XRFS.

This section deals with mineral sands containing zircon, ilmenite and rutile, and with the analysis of Ti-slugs. The analysis of titanomagnetite is described in Chapter 23, Section 23.3, and the determination of Sn in Section 18.3. Section 18.4 describes the analysis of monazite and other REE-bearing samples.

Zircon is mainly used as an opacifier in the decorative ceramics industry, in foundry sands, abrasives and for the production of ZrO_2 and Zr metal. Ilmenite, rutile, anatase, leucoxene and Ti-slag are processed mainly to TiO_2 pigment, used in paints, plastics, ceramics and paper production, and for reduction to Ti metal. Garnet is used as an abrasive and may be analysed as a silicate (Chapter 16, Section 16.6).

18.2.2 Sample preparation

Pressed powder pellets are suitable for exploration and mine and plant control, where a rapid turnaround of analysis is important. See Chapter 2, Section 2.4.2 for information on the preparation of pressed powder pellets.

Fused beads are the industry standard preparation method for analyses where greater accuracy is required. A dilution of 1:9 sample:flux is suitable for zircon and ilmenite, but high Ti samples, such as rutile (and related leucoxene and anatase), require a higher dilution, and 1:19 has been shown to be successful. 12:22 flux is a good general flux for these samples, but a range of flux mixtures is in use in laboratories, and experimentation is necessary to determine which is the most suitable for each project and the equipment at hand.

All the fractions should be pulverised as finely as is practical, to at least 100% <75 μm . Oversize particles may not dissolve completely and will crack the bead on cooling. Zircon is slow to dissolve and a higher fusion temperature and longer fusion time are necessary. A higher dilution may also be necessary. Agitation is essential for all of the materials discussed in this section. Care should be taken on cooling of the beads, as recrystallisation of zircon and of rutile can occur. The use of ammonium iodide as releasing agent is essential, but use as little as possible (about 0.01g before fusion or 0.001g just before pouring) as $IL\beta_2$

Chapter 19: Precious metals

19.1 INTRODUCTION

In the determination of precious metals X-ray fluorescence spectrometry is used mainly for the analysis of alloys, concentrates and automotive catalysts. Both wavelength and energy dispersive instruments are used. XRF spectrometry is also used to measure Au, Ag and base metals in hydro-metallurgical plant activated carbon.

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19.7 Pt, Pd AND Rh IN USED AUTOMOBILE CATALYTIC CONVERTERS

Since the 1990s, the automotive industry has become the largest consumer of Pt, Pd and Rh, which are used in catalytic converters in car exhaust systems. Of total world production in 2012, 40% of the Pt, 74% of the Pd and 80% of the Rh were consumed by the auto catalyst industry (Johnson Matthey, 2012).

A catalytic converter generally consists of the catalytically active metals, Pt, Pd and Rh, deposited, using a CeO_2 , BaO or ZrO_2 wash-coating, on a large surface area of a substrate, such as alumina or cordierite ($(\text{MgFe})_2\text{Al}_4\text{Si}_5\text{O}_{18}$) pellets or honeycombed monolith. Alternatively, corrugated steel foil is used to form a honeycombed metal substrate. The pellets, monolith or foil are contained in a metallic case, coupled to the vehicle exhaust system, to convert the toxic carbon monoxide (CO) and nitrogen oxides (NO_x) to CO_2 , H_2O , O_2 and N_2 . Various ratios of Pt, Pd and Rh are used, dependent on the type and size of engine. Pt and/or Pd are used for hydrocarbon and CO oxidation, while Rh is used for NO_x reduction.

The precious metals are reclaimed from used catalytic converters. In the recovery process, the entire substrate is pulverised or shredded and the precious metals are extracted by pyro- or hydro-metallurgical techniques (Rumpold and Antrekowitsch, 2012).

The conventional analysis of the substrate is by aqua regia extraction of the PGEs followed by AAS or ICP-AES, or by peroxide fusion, dissolution and ICP-AES (Pitre and Bédard, 2013). However, XRF is ideally suited to the analysis of PGMs in new or used catalytic converters, and requires minimal sample preparation beyond pulverisation or shredding.

19.7.1 Sample preparation

Because the wash-coating encloses the ceramic substrate, fine pulverising is essential to expose the substrate and ensure homogenisation. As shown in Figure 19-4, optimum pulverising time must be found by increasing the time in steps until a plateau is reached. Steel substrates are shredded and the wash-coat carrier, which is brittle, is separated physically and pulverised. A magnet may be used to remove steel particles before pulverising. The loose powders may be measured in a plastic liquid cell in a helium atmosphere (never in a vacuum), or pressed to form pellets (see Chapter 2, Section 2.4.2 for more information).

Chapter 23: Iron Ore and associated Iron- and Steel-making Slags

23.1 INTRODUCTION

This chapter sets out methods of XRF analysis of a wide range of iron ore types, including haematites, goethites, limonites, magnetites and titanomagnetites, and associated iron and steel making slags.

The methods discussed are suitable for a wide range of ore grades (high grade to reject) and products from associated steel making processes (blast furnace/converter, electric arc and direct reduction).

23.2 IRON ORES

Some iron ore deposits contain significant concentrations of iron sulphides, for example "black shale" associated with some deposits in the Pilbara, Western Australia. The detection of black shale is an important safety issue for mine blasting operations. Care must also be taken to prevent platinum ware damage during preparation of fused beads of ores containing sulphides.

In addition, some deposits may contain quite high levels of other metallic elements, e.g. percentage levels of manganese. Titanomagnetites often contain significant levels of other transition elements such as Cr and V. Certain iron ore bodies in the Pilbara region of Western Australia contain percentage levels of boron from tourmaline minerals. It is important that the analyst has a good understanding of the expected sample compositional range prior to setting up an analytical method.

23.2.1 Sample preparation

Fused beads (see also Chapter 2, Section 2.4.5). A basic flux containing a significant portion of lithium metaborate is required for iron ores. Flux type 12:22 (35% lithium tetraborate : 65% lithium metaborate) is widely used in Australian laboratories. Other lithium tetraborate/lithium metaborate flux mixtures up to and including a 57:43 mix may be used. Generally sample to flux ratios in the range 1:8 to 1:10 are used. It is recommended that the sample particle size be reduced to 100% less than 105µm prior to weighing for fusion.

Samples may be dried (110°C for a minimum of 2 hours) or a concurrent moisture determination carried out on a laboratory air-equilibrated sample. If dried samples are used, then the samples must be weighed for fusion as soon as possible after removal from the drying oven. Iron ores, in particular goethitic types, absorb moisture rapidly after drying. For the highest accuracy analysis, the concurrent moisture determination approach is recommended.

Many iron ores contain reduced species, for example FeO, sulphides, etc., that can damage platinum ware during fusion. Pre-oxidation by roasting or the use of

29.4 LUBRICATING OILS

These are an extension of the pure oils mentioned above. They have various additives so as to meet the requirements for machinery lubrication, and thus wear prevention, under many different operating conditions (Figure 29-8).

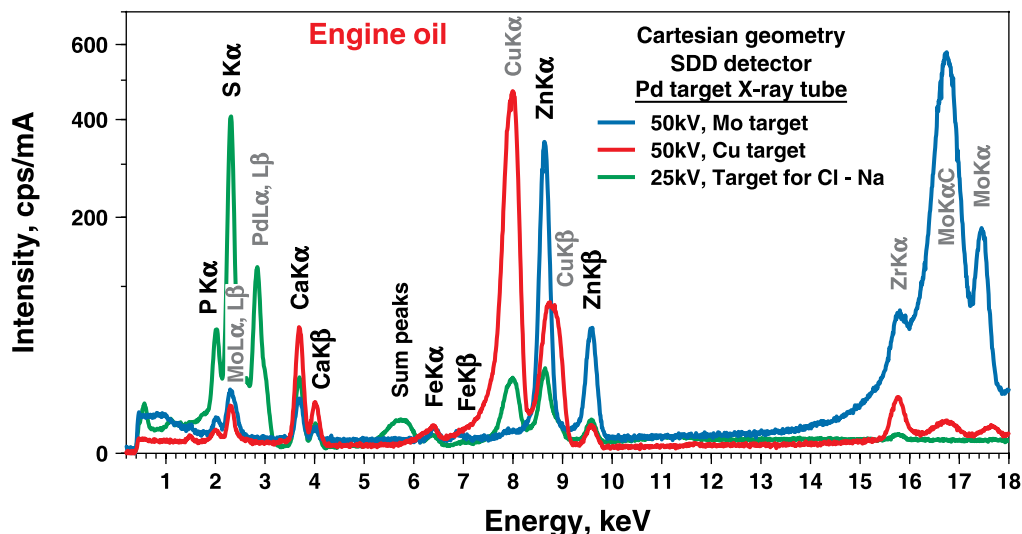


Figure 29-8. EDXRF scans of a motor oil showing the presence of P, Ca, and Zn as additives.

Additives are substances that improve the anti-friction, chemical and physical properties of base oils, thus enhancing the lubricating performance of the oil and extending the equipment life. The combination of different additives and their quantities are determined by the type of lubricant (engine or gear oils, hydraulic oils, cutting fluids, compressor oils, etc.), the specific operating conditions (temperatures, loads, contamination levels, etc.) and the need to extend the intervals between oil changes.

29.4.1 Sample preparation

Sample preparation is similar to that discussed in Section 29.3.1, and the same comments apply.

29.4.2 Analyte elements

Analyte elements are listed in Table 29-3.

Table 29-3. Analyte elements - Lubricating oils.

Main elements: Zn, Ba, Ca, S, P
Other elements of interest: Mo, K, Cl, Si, Mg, Na
Elements as internal standards (if required): Sn, Pb, Ni, Ti

29.4.2.1 WDXRF