

X-ray Fluorescence Spectrometry

X-ray Fluorescence Spectrometry (XRF) is a non-destructive, quantitative technique for determining chemical composition. When a primary x-ray collides with an atom in the sample, the energy of the x-ray may be absorbed. If the x-ray quantum has sufficient energy, it displaces an electron from one of the inner shells and the atom becomes ionized. When an electron from the outer shell fills that vacated position, a secondary X-ray with a wavelength characteristic of that element is emitted. The number of secondary x-rays emitted at each wavelength is proportional to the amount of each element present in the sample.

In general, XRF can detect any element heavier than $Z=4$ (Be) in the periodic table. Detection limits depend on the analyte (with lighter elements being less sensitive) and the matrix of the sample, but a detection limit of 10 - 100 ppm or better is frequently achievable. While the analysis itself is non-destructive, some sample preparation techniques destroy the sample form. Most prepared samples can be saved indefinitely for re-checks or additional XRF analysis. Although liquid analysis is possible, analysis of solids and powders is by far the most common. Materials, such as alloys, minerals, organic and inorganic chemicals, refractories, and ceramics, can be quickly analyzed.

While XRF is an excellent quantitative tool, it can also be used to produce qualitative elemental data. Scanning across the wavelength spectrum will indicate elemental presence and the data can then be used to provide relative comparisons between samples. Semi-quantitative analysis capability has been recently added to enhance the analysis of unknown materials. Major constituents can be qualitatively determined on milligram size samples.

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The following sections detail the XRF analytical services that are routinely provided. Method development and other services are available upon request.

STD OXIDE (Includes LOI) - also referred to as Fusion and Std Fusion

The calibration and specimen preparation methods used to develop this method allow for a wide variety of sample types and sizes. Specimen preparation involves dissolving a portion of the sample in a lithium tetraborate flux at 1000°C in platinum crucibles. The resultant solid solution is cast as a glass bead to be analyzed. Special preparation methods may be required to produce accurate quantitative results for some sample types.

Please consult with or notify the XRF analyst if the following materials may exist in your specimen: Elements in the metallic state, carbides, >0.5% B or Li compounds, >5% elemental carbon such as Graphite, > 1% compounds in a reduced state such as FeO or metal sulfides.

All quantitative results from this method originate from calibrations using internationally recognized Certified Reference Materials, high purity reagent chemicals, and combinations thereof. All results, unless specifically noted, are the measured total elemental concentration in the specimen. All results reported by the XRF technique have been measured as the element. Major and minor components are typically reported the most common oxide (i.e. %Si as %SiO₂) for the convenience of our customers. All reported results are the average of duplicate specimen preparations unless otherwise noted.

Types of Samples	Sample Size
Silicate Minerals (talc, clays, geological materials, etc.)	10 - 20 g
Alumino-silicates	3 g minimum
Magnesia	*
Refractories (not including SiC bearing)	If less than 3g
Cement, Slag	available
Lime "grit", "scale", hydrates	contact the
Gypsum and related minerals	XRF Analyst
Paper ash, DIR, coating pigments	
Zircon	
Rutile and Anatase	

- - When very small samples are all that is available, there are special preparation and analysis techniques available that can use as little as 0.15g to produce quantitative results with slightly elevated limits of quantitation. Contact the XRF primary analyst.

Results provided with STD OXIDE:

Analyte Element as Oxide	Analysis Range	Limit of quantitation
Al ₂ O ₃	0 - 100%	0.1%
BaO	0 - 60%	0.05%
CaO	0 - 100%	0.05%
Cr ₂ O ₃	0 - 15% *	0.05%
Fe ₂ O ₃	0 - 100%	0.05%
K ₂ O	0 - 16%	0.02%
Mn ₂ O ₃	0 - 15% *	0.05%
Na ₂ O	0 - 30%	0.05%
P ₂ O ₅	0 - 40%	0.05%
SiO ₂	0 - 100%	0.2%
SrO	0 - 3%	0.05%
TiO ₂	0 - 60%	0.05%
WC	0 - 5% **	0.05%
ZrO ₂	0 - 35%	0.05%
LOI	0 - 100%	0.05%

* levels to 60% can be analyzed by dilution methods

** if the specimen is pulverized in a tungsten carbide mill during our preparation process, the tungsten content is calculated out of the bulk analysis and the reported results have been back-calculated to an “as received” basis. If specimen was pulverized in a tungsten carbide mill, all tungsten is assumed to have been introduced during grinding. A comment in the results table will accompany all specimens calculated this way.

The following table lists elements analyzed but only reported if their concentration is significant to the customer’s request:

Analyte Element as Oxide	Analysis Range	Limit of quantitation
CoO	0 - 1%	0.01%
CuO	0 - 1%	0.01%
HfO ₂	0 - 12%	0.05%
MoO ₃	0 - 20%	0.05%
Nb ₂ O ₃	0 - 1%	0.02%
NiO	0 - 1%	0.01%
Rb ₂ O	0 - 0.2%	0.02%
Sb ₂ O ₃	0 - 1%	0.02%
SnO	0 - 1%	0.02%
SO ₃ ***	0 - 50%	0.05%
ThO ₂	0 - 1%	0.02%
U ₃ O ₈	0 - 0.1%	0.02%
V ₂ O ₅	0 - 1%	0.02%
Y ₂ O ₃	0 - 1%	0.02%
ZnO	0 - 10%	0.02%

*** - Most Sulfur compounds are volatilized during normal specimen preparation. A modified preparation method can be used such that at least 98% of the sulfur present can be retained and quantified. The requestor should specify if sulfur is known to be present and should be quantified.

STD CaCO₃

This method was specifically developed for the analysis of limestone and PCC. Calcium and calcium-magnesium carbonates in natural or precipitated form can be analyzed with this method.

All quantitative results from this method originate from calibrations using internationally recognized Certified Reference Materials, secondary reference materials validated by internal or external laboratories and combinations thereof. All results, unless specifically noted, are the measured total elemental concentration in the specimen. All results reported by the XRF technique have been measured as the element. Major and minor components are typically reported the most common oxide (i.e., %Si as %SiO₂) and trace elements are reported as the element (i.e., ppm Ba) for the convenience of our customers.

Types of Samples	Sample Size
Limestone, calcitic, and dolomitic PCC, coated and uncoated	10 - 50 g Consult if <30g

Analysis Results provided with STD CaCO₃

Analyte Element/Oxide	Analysis Range	Limit of quantitation
%Mg	0 - 13%	0.03%
%Mg as %MgO	0 - 22%	0.05%
%Si	0 - 3%	0.01%
%Si as %SiO ₂	0 - 7%	0.02%
%Al	0 - 0.8%	0.01%
%Al as %Al ₂ O ₃	0 - 1.5%	0.02%
%Ca	22 - 40%	22%
%Ca as %CaO	30 - 56%	30%
%Fe	0 - 1.4%	0.001%
%Fe as %Fe ₂ O ₃	0 - 2%	0.002%
Mn	0 - 5000ppm	10ppm
%Mn as %Mn ₂ O ₃	0 - 0.7%	0.002%
Sr	0 - 5000ppm	10ppm
%Sr as %SrO	0 - 0.6%	0.002%
%K	0 - 0.25%	0.01%
%K as %K ₂ O	0 - 0.3%	0.01%
Ti	0 - 1000ppm	10ppm
%Ti as %TiO ₂	0 - 0.2%	0.002%
%P	0 - 1.5%	0.005%
Zn	0 - 500ppm	10ppm
%W as %WC	0 - 0.5%	0.05%
%S	0 - 0.5%	0.01%

STD CaCO₃ continued

The following table lists elements analyzed but only reported if their concentration is significant to the customer's request:

Element	Analysis Range	Limit of quantitation
%Na as %Na ₂ O	0 - 0.5%	0.02%
Cu (ppm)	0 - 1000ppm	5ppm
Ga (ppm)	0 - 200ppm	10ppm
As (ppm)	0 - 200ppm	2ppm
Y (ppm)	0 - 200ppm	10ppm
Zr (ppm)	0 - 200ppm	5ppm
Nb (ppm)	0 - 200ppm	10ppm
Mo (ppm)	0 - 200ppm	10ppm
Ba (ppm)	0 - 5000ppm	20ppm
Pb (ppm)	0 - 100ppm	2ppm

Qualitative and Semi-Quantitative Scans (also known as SemiQ scans)

This method was developed for the analysis of unknown materials to provide a “snapshot” of elemental composition. Using this method samples can be analyzed to detect the presence of elements heavier than Nitrogen ($Z > 7$). Scan data can be used to compare one specimen to another to provide relative information. Scan data can also be used to provide semi-quantitative results when compared to Certified Reference Materials known to be of similar composition or when applied to a calibration produced from scans of reference materials with known concentrations.

Types of Samples	Sample Size
Qualitative: Nearly any sample type that will not decompose or volatilize below 60°C or when exposed to high levels of radiation Semi-Quantitative; Inorganic powders or solids that can be presented as a flat homogeneous surface and Organic solids that have a known or approximate C and H content.	either smaller than 40mm X 40mm X 40mm or can be cut to fit into a sample holder, 20ml of liquids, 3g of powders

Note: The sample sizes listed are preferred. Samples as small as 0.1mg or a single drop of liquid can be used to provide qualitative results however the samples used for analysis are not recoverable for other testing.

BARITE

(Barytes, BaSO₄)

This method was specifically developed for the analysis of Barite ore and finished products.

All quantitative results from this method originate from calibrations using high purity reagent chemicals, internationally recognized Certified Reference Materials, and combinations thereof. All results, unless specifically noted, are the measured total elemental concentration in the specimen. All results reported by the XRF technique have been measured as the element. Major and minor components are typically reported the most common oxide (i.e. %Si as %SiO₂) convenience of our customers. Specimen preparation involves dissolving a 0.7g portion of the sample in a 66% lithium tetraborate/34% lithium metaborate flux at 1000°C in platinum crucibles. The resultant solid solution is cast as a glass bead to be analyzed. Minimum sample size is 1g but 10-20g is preferred.

Analysis Results provided by ASG-XRF -105 (Barite)

	Analysis range	Limit of Quantitation	Uncertainty (95% confidence, k=2)
%Al as %Al ₂ O ₃	0.01-4	<0.01	0.10
%Ba as %BaO	48-66	NA	0.32
%Ca as %CaO	0.01-8	<0.01	0.04
%F	0.05-3	<0.05	0.07
%Fe as %Fe ₂ O ₃	0.01-1.2	<0.01	0.01
%K as %K ₂ O	0.01-1	<0.01	0.002
%Mg as %MgO	0.05-5	<0.05	0.01
%Mn as %Mn ₂ O ₃	0.01-0.1	<0.01	0.01
%Na as %Na ₂ O	0.05-2	<0.05	0.02
%P as %P ₂ O ₅	0.01-0.1	<0.01	0.01
%Si as %SiO ₂	0.01-12	<0.01	0.04
%S as %SO ₃	26-35	NA	0.60
%Sr as %SrO	0.01-1.2	<0.01	0.01
%Ti as %TiO ₂	0.01-0.1	<0.01	0.02
%Zr as %ZrO ₂	0.01-0.1	<0.01	0.01

SLAG

This method was developed to provide a rapid, more cost effective analysis technique for providing elemental analysis of steelmaking slags. Industrial or laboratory produced slags such as EAF, BF, BOF, Ladle, and Tundish slags can be analyzed by this method. If an analyte requested is not included in this method it can be determined either by semi-quantitative scans or using the STD OXIDE method (with suitable precautions taken to insure complete oxidation).

All quantitative results from this method originate from calibrations using internationally recognized Certified Reference Materials. All results, unless specifically noted, are the measured total elemental concentration in the specimen. All results reported by the XRF technique have been measured as the element. Major and minor components are typically reported the most common oxide (i.e., %Si as %SiO₂) and trace elements are reported as the element (i.e., %F) for the convenience of our customers. Sample preparation involves the removal of metallic contaminants, crushing, grinding to a fine powder, and pressing of the powder into a 31mm pellet. Minimum sample size is 10g but 20-30g is preferred. If <10g sample is available, slags will be analyzed by the STD OXIDE method. Analysis Results provided by XRF Slag

	Analysis Range	Limit of Quantitation (%)
%Al as Al ₂ O ₃	0.5% - 15%	0.2
%Ca as CaO	2% - 60%	1
%Cr as Cr ₂ O ₃	0.05% - 30%	0.05
%F	0.01% - 8%	0.1
%Fe as Fe ₂ O ₃	0.2% - 45%	0.5
%K as K ₂ O	0.2% - 1.3%	0.1
%Mg as MgO	1.5% - 25%	0.5
%Mn as MnO	0.02% - 13%	0.05
%Na as Na ₂ O	0.03% - 0.9%	0.05
%P as P ₂ O ₅	0.01% - 9%	0.05
%Si as SiO ₂	9% - 57%	2
%S	0.01% - 1.5%	0.05
%Ti as TiO ₂	0.16% - 2.5%	0.05
%V as V ₂ O ₅	0.05% - 0.75%	0.05

MAGNESITE (MgCO₃)

This method was specifically developed for the analysis of Magnesite ore and kiln feed for the production of refractory grade Magnesia (MgO).

All quantitative results from this method originate from calibrations using high purity reagent chemicals, internationally recognized Certified Reference Materials, and combinations thereof. All results, unless specifically noted, are the measured total elemental concentration in the specimen. All results reported by the XRF technique have been measured as the element. Major and minor components are typically reported the most common oxide (i.e. %Si as %SiO₂) convenience of our customers. Specimen preparation involves dissolving a 1.5g portion of the sample in a 66% lithium tetraborate/34% lithium metaborate flux at 1000°C in platinum crucibles. The resultant solid solution is cast as a glass bead to be analyzed. Minimum sample size is 2g but 10-20g is preferred.

Analysis Results provided by XRF Magnesite

	Analysis Range	Limit of Quantitation (%)	Uncertainty at range average (95% confidence, K=2) (%)
%Al as %Al ₂ O ₃	0.02% - 6%	0.02	0.02
%Ba as %BaO	0.05% - 0.7%	0.05	0.02
%Ca as %CaO	0.05% - 5%	0.05	0.05
%Cr as %Cr ₂ O ₃	0.01% - 0.5%	0.01	0.01
%Fe as %Fe ₂ O ₃	0.01% - 6%	0.01	0.02
%K as %K ₂ O	0.03% - 0.7%	0.03	0.01
%Mg as %MgO	28% - 48%	28	0.2
%Mn as %Mn ₂ O ₃	0.01% - 0.7%	0.01	0.02
%Na as %Na ₂ O	0.05% - 0.7%	0.05	0.05
%P as %P ₂ O ₅	0.02% - 0.7%	0.02	0.01
%Si as %SiO ₂	0.05% - 20%	0.05	0.1
%S as %SO ₃	0.05% - 0.4%	0.05	0.05
%Sr as %SrO	0.01% - 0.7%	0.01	0.01
%Ti as %TiO ₂	0.01% - 0.7%	0.01	0.02

INK ON PAPER

These methods were developed specifically for our Printing research group to provide rapid analysis of printed paper samples using the concentration of an element associated solely with the ink pigment to provide a quantitative measure of ink coverage. All quantitative results are based on calibrations using secondary reference materials with values determined by total digestion analysis by ICP-MS. Currently there are two methods; one based on Cu and the other based on Co. The Cu method is restricted to the analysis of SC and LWC papers printed with Cyan inks that contain the pigment Copper Phthalocyanine blue. The Co method is restricted to SC and LWC papers printed with Black ink that has been doped with a Cobalt solution (tracer). The methods can be extended to other inks and papers provided the element of interest is either added or unique to the ink pigment, it is not present in the filler or coating pigment (unless unprinted blanks are provided), and the element is measurable in the X-ray spectrum and can be quantified by a secondary technique such as ICP, AA, INAA, or similar.

The results are reported as the element in units of $\mu\text{g}/\text{cm}^2$ to provide the client with data that can be translated to grams of ink per square meter of paper when the concentration of the element sought has been measured in the actual ink used to print the paper. Otherwise, the data are only relative within a given set of printing conditions. Data can be reported as $\mu\text{g}/\text{g}$ if requested.

Contact the XRF primary analyst for further details on analysis range and uncertainty.