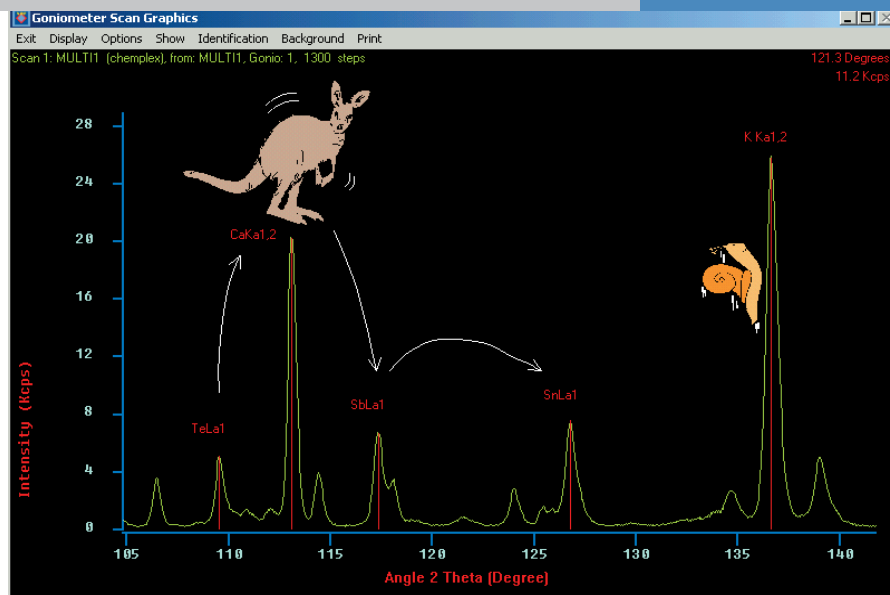


UniQuant® is an analysis package for standardless semi-quantitative to quantitative XRF analysis using the intensities measured by a sequential X-Ray spectrometer. It represents a completely new method in XRF analysis.

UniQuant 5

Program for semi-quantitative to quantitative XRF analysis using Thermo Scientific ARL WDXRF & EDXRF Spectrometers



UniQuant uses "peak hopping" to acquire intensities for up to 133 line positions

Introduction to UniQuant®

As its name suggests, it Unifies all types of samples into one and the same analytical program and it is Unique in that respect. Thermo Scientific UniQuant program is highly effective for analysing samples for which no standards are available. Sample preparation is usually minimal or not required at all. Samples may be of very different natures, sizes and shapes.

Elements from F up to Am (or their oxide compounds) are analysed in samples like a piece of glass, a screw, metal drillings, lubricating oil, loose fly ash powder, polymers, phosphoric acid, thin layers on a substrate, soil, paint, the year rings of trees and in general those samples for which no standards are available.

Elements Be to O can also be analyzed in some applications providing that the required crystals are installed on the instrument.

The reporting is in weight% along with an estimated error for each element.

UniQuant® 1, 2, 3, 4 and 5

UniQuant 1 was introduced in spring 1989. The last update was 1.76. The program was for 53 elements and gave semi-quantitative to quantitative results.

UniQuant 2 was introduced in 1992. The last update was 2.53. The program deals with 77 elements. A lot of features were added for convenience and speed of operation.

UniQuant 3 was introduced in September 1995. The last update was 3.26. Interelement corrections are coped with by employing the method of (Extended) Fundamental Parameters (FP). As a result, for major and minor concentrations, UniQuant 3 provides the highest possible analytical accuracies achievable in X-Ray spectrometry. Such high accuracies only apply to perfectly homogeneous samples like glass, beads, oils, polymers and many (but not all) types of alloys.

Like UniQuant 1 and 2, UniQuant 3 works under DOS.

UniQuant 4 was introduced in September 1997, starting with version 4.01. It is a 32 bit program and works under Windows® 2000 or XP environment. Trace analysis has been perfected by improved background calculations, which are supported by interactive plots of the calculated background continuum and spectral impurities.

Analyte elements Pu and Am have been added.

UniQuant 5 has been introduced in February 2001. It works under Windows 95, 98 or Windows NT or 2000 environment. It brings a number of facilities to the analyst, notably the following:

- A new calibration (« daughter calibration») can now be easily derived from the original calibration (« parent calibration »), thus enabling to make calibrations which are specific to given matrices in order to further improve the accuracy of analysis
- More flexibility in the definition of compounds and possibility to use two XRF results to deduce compound concentrations through calculation or to calculate a surplus as element or oxide. This leads to more accurate results for example for sulphides and stearates
- As specific filters can be used to modify the X-ray excitation, any such tube filter can now be specified per group of XRF lines
- All data specific to a given user are contained in one folder, which allows easy exchange of data for example by e-mail

The total number of analyte elements is 79. In that case the number of analyte XRF lines is 135 (2 extra alternative lines were added).

UniQuant 5 as a product

UniQuant is a PC program comprising:

- A licence for the use of the UniQuant program
- A CD-ROM with the UniQuant program, data files and user's manual

- An extensive on-line description with amongst others :
 - instructions for setting up the spectrometer
 - instructions for initial calibration and maintenance
 - handling of unknown samples
 - the theory
- A set of 11 calibration samples for initial setting-up and for maintenance
- Some small hardware, such a centring rings, to facilitate sample presentation
- A file containing the calibration parameters as defined in the factory
- On option, a set of 53 pure element samples is available. The total of 64 samples are used for factory calibration of UniQuant 5

UniQuant is fully pre-installed at the factory and calibrated for elements fluorine (Z=9) to americium (Z=95) on the goniometer of the ARL ADVANTX Series or ARL 9900 Series spectrometers ensuring a constant high quality of analytical results. On special request, ultra-light elements can be calibrated for specific matrices if the appropriate crystals are installed.

Why to use UniQuant?

In general terms, UniQuant is used to provide:

- A **quantitative** analysis if **no standards are available**
- A **quantitative** analysis with highest accuracy if **standards are available**. About 50 % of the current UniQuant users (about 500) only use UniQuant and do not use conventional XRF analysis (calibration by regression). Part of them had little choice because no standards are available (waste materials, polymers). But there is also a tendency by many users to replace the conventional method by UniQuant using standards to firm it up for 'families' of samples
- Determination of the % sulphur present as **sulphide** (reported as % S) and the % sulphur present as **sulphate** (reported as % Sx)
- Determination of the % phosphor present as **phosphide** (reported as % P) and the % phosphor present as **phosphate** (reported as % Px)

- An analysis of **small** and/or **odd shaped** samples
- An analysis of a **thin composite layer**, along with the mass / area. The layer may be on a substrate containing some elements that are also in the layer. Or, the layer may be on a 'neutral' substrate, like with dust on a filter.
- The determination of the masses of layers in a **multi-layer** structure, usually on a substrate
- **Screening** samples and detection of unexpected elements
UniQuant supports **79 elements**.
- A **fast pre-analysis** of totally unknown samples prior to decide on further analyses
- A chemical analysis to **support phase analysis by X-ray diffraction**

Major features

UniQuant is set up as standard for the analysis of 74 + 2 elements (F to Am). The extra 2 are for the element "Sx", Sulphur present as sulphate as opposed to the element "S", sulphur in sulphide and the element "Px", phosphor as phosphate as opposed to elemental "P" present as phosphide.

Ultra-light elements Be to O can also be analyzed in some applications providing that the necessary crystals are installed on the instrument. These elements require a matrix specific calibration.

Table 1 shows which 79 elements may be analyzed by UniQuant.

Table1 :
Bold: Analyzed Elements
Italic: not known by UniQuant

Elements analyzed																			
H																	He		
Li	Be													B	C	N	O	F	<i>Ne</i>
Na	Mg													Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	<i>Kr</i>		
Rb	Sr	Y	Zr	Nb	Mo	<i>Tc</i>	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	<i>Xe</i>		
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	<i>Po</i>	<i>At</i>	<i>Rn</i>		
<i>Fr</i>	<i>Ra</i>	A																	
		L	La	Ce	Pr	Nd	<i>Pm</i>	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
		A	<i>Ac</i>	Th	<i>Pa</i>	U	<i>Np</i>	Pu	Am	<i>Cm</i>	<i>Bk</i>	<i>Cf</i>	<i>Es</i>	<i>Fm</i>	<i>Md</i>	<i>No</i>	<i>Lr</i>		

UniQuant calculates absorption by H and Li. Argon has been included because it may be found in materials made under an Argon atmosphere.

Nature of samples

As stated above, the unknown samples may take a great variety of physical forms such as:

- A solid disk of metal or a synthetic material
- A multi-element mono-layer on a substrate
- A mono-element multi-layer on a substrate
- A small piece of solid sample placed on a supporting film
- A pressed powder that may include a binder
- A very small amount of powder on a supporting film
- A solid solution of a mineral (a glass bead)
- A liquid sample from a small drop to a full cup
- A filter aerosol sample

Analysis time

A totally unknown sample may be measured by the prescribed measuring channels (120 spectral positions) for determination of 74 + 2 elements (F to Am). The spectrometer time then is about **14 minutes**.

Ultra-light elements can be included in special applications with specific calibration and crystals. When included the spectrometer time is about **18 minutes**.

Samples belonging to a known family may be measured by a smaller sub set of the full set of measuring channels. For example, the analysis of routine waste disposal samples may be limited to say 55 measuring channels with extra long measuring times for relevant traces. The spectrometer time can then be as low as **5 minutes**.

Accuracy for majors and minors

The accuracy for concentrations higher than 1 weight % primarily depends on the physical nature of the sample. The errors are smallest for thick full-area homogeneous samples and are quite acceptable for less favourable physical conditions. As a rule of thumb, the standard error in weight % for a major or minor constituent is equal to

$$\text{StdErr in Wt \%} = K \cdot \sqrt{\%C - \frac{\%C}{100}}$$

where $K=0.05$ to 0.15 depending on the element and the physical nature of the sample.

UniQuant is intended to cover the widest possible concentration ranges while using one single set of calibration data. Here we are not thinking about a wide range of alloys or of oxide samples. The range that we mean includes samples like oils, polymers, beads, thin layers and all types of alloys! Errors are smallest for thick full-area homogeneous samples and are quite acceptable for less favourable physical conditions.

For specific applications, where very high accuracy is required, UniQuant may use specially calibrated data sets, for example one for Alloys and one for Beads or Glass.

Then international or own standards are used to firm up the calibration. This way of working may lead to the same high accuracy as with conventional analysis using regression analysis of standards. Although using specialized data sets has not been the primary philosophy behind UniQuant, its application allows replacing conventional methods by the UniQuant method with far less specialized analytical programs. Several UniQuant users have indeed done so.

Trace analysis

Precision

Precision (reproducibility) of the analysis of a given sample specimen depends only on counting statistics. For each analyzed element, UniQuant reports the Standard Deviation (Sigma) in ppm which takes into account counting precision and the corrections that have been applied for background and line overlaps.

For large (full area) samples that are not or not highly diluted, the Sigma's are surprisingly small, for example 1 or 2 ppm for measuring times of 4 or 10 seconds per analytical line. The Sigma is smallest with lighter matrix samples, for higher atomic numbers and with longer measuring times.

Trace elements (with $Z > 20$) in heavier matrices can be well determined from 20 ppm onward. For light matrix samples like polymers, this value is 5 ppm or even lower.

Accuracy

The accuracy for traces is depending on the quality of the corrections made for:

- **Background** well done by UniQuant.

- **Spectrometer's spectral impurities** well done by UniQuant.
- **Spectral line overlaps** uniquely solved by UniQuant. **Very important !**
- **Matrix effects** solved by FP (Fundamental Parameters)
- **Physical effects** UniQuant has unique ways to compensate for certain physical effects.

Interactivity

UniQuant has been designed for a maximum of interactivity. A pre-condition is speed of entering data and speed of calculation. The user interface has been designed for an absolute minimum of key strokes or mouse operations.

The need for fast interactivity is illustrated by the following example:

UniQuant evaluates a totally unknown powder sample in a first calculation (5 seconds) for which the analyst assumes that a mineral sample consists of oxides. The results however may show a very high content of sulphur. The analyst concludes that the sample is a sulphide ore. This means that elements like Pb, Zn, Fe, Mo are as sulphide whilst elements like Si and Al occur as oxides. The original assumption would assume most elements to be as oxides, even sulphur. The sum of concentrations would end up at a level higher than 100 %. Now, the analyst just changes Oxides to sulphides in the input of the General Data table and starts a second calculation. All this is a matter of a few seconds only.

Thin layer samples

Mono-layer samples

UniQuant can calculate the sample mass along with its associated standard deviation.

At the same time the composition of the layer is calculated.

If the layer is on a substrate with elements that are also in the layer, UniQuant can take their effect into account.

Multi-layer samples

UniQuant may calculate the masses of the layers in a multi-layer structure.

Batch modes

In order to short-cut a lot of work at the PC, batch modes are provided. These may be used for evaluation of calibration (set-up) samples as well as for evaluating a suite of unknown samples. Samples are 'tagged' in a directory and the 'process' is started.

Reporting

The results of calculations are in terms of % and ppm and can be viewed at the screen or printed in a comprehensive form that appeals to the analyst. This form can be saved on disk in ASCII or re-directed to a specified file on disk, which can easily be picked up by any word processor or spreadsheet program.

In addition, a report can be printed in a standard form (in the order of atomic number) that is intended for the analyst's client where elements (and oxides) are presented in the order of atomic number Z, or listed in descending order of concentration, or in alphabetic order of element names.

Each reported concentration is accompanied by a 'StdErr'. The practical confidence interval is ± 2 StdErr.

A joint table of results can also be designed in order to have results of a suite of samples in one common table.

UniQuant's principles

UniQuant is based on a state of the art science of X-ray spectroscopy. In addition, it makes use of completely new methods that hitherto have not been published.

Specially developed DJ Kappa Equations are employed. Kappas are "intrinsic" spectrometer sensitivities (which are independent of samples).

Interelement corrections are made by means of so-called "effective Mass Absorption Coefficients" which have been calculated from Fundamental Parameters, including the primary spectrum. The use of these coefficients dramatically speeds up the calculation times since with this method, time consuming integrations over the primary spectrum from $_min$ to $_edge$ are not required.

A new approach is applied for background and spectral line overlap corrections.

The counting statistical errors are calculated for all elements and reported in ppm. The reported errors include also those due to line overlap corrections (propagation of errors).

UniQuant corrects the attenuation of intensities that occur if a sample supporting film is used and if the measurement is performed in a He atmosphere.

UniQuant allows the user to input a priori knowledge about the sample, such as % rest, the dilution, the sample area, the

sample's mass / area and the sample's chemical nature. The latter may be Elemental, Oxides, Sulphides, Alkalies or Ionic. The calculations and reporting are done accordingly.

The user may ask UniQuant to calculate the % **rest**, the **dilution**, the effective analyzed **area** or the **mass / area** (in mg/m²) in case he is in doubt about the actual value.

XRF spectrometer + UniQuant, an overview

UniQuant needs 120 intensities as measured by 120 channels of which the instrumental parameters are prescribed by UniQuant.

These parameters are kV, mA, tube filter, internal aperture, collimators, detectors and settings of the Pulse Height Discriminator. The intensities are written in a file on hard disk by the spectrometer's software. UniQuant works from there on. Thus the interface between the spectrometer system and UniQuant is only the hard disk.

Thanks to Microsoft's Windows environment, the user can run both WinXRF/OXSAS and UniQuant simultaneously.

For each unknown sample, the user must specify at the PC's keyboard the so-called "General Data" of the sample. These are geometrical data such as the analyzed area (if known) and the physical data such as the mass per unit area (if known), the dilution factor (if relevant and if known).

UniQuant® in historical perspective

The first X-ray spectrometers introduced in the fifties were primarily used for qualitative and semi-quantitative analysis. The recorded spectrogram was extensively used for this purpose. Soon, quantitative analysis was done as well. It was based on type standards analysis, which means by comparison with "close" standards.

Much later, at the end of the sixties with the advent of minicomputers, the emphasis shifted almost completely to quantitative analysis.

The number of standards required was reduced to a few through the use of mathematics that used fundamental parameters to calculate interelement correction factors in advance (Alphas).

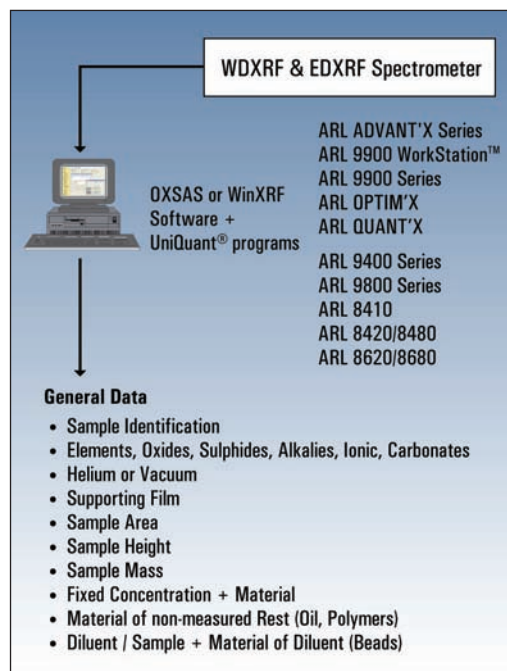
Meanwhile, for various reasons, the role of XRF in qualitative and semi-quantitative analysis had decreased to a record low.

This work was then partly taken over by Energy Dispersive XRF spectrometers. The limitation of the latter is in the resolution and in a low total intensity allowed at the detector. As a result, its use is restricted to the analysis of major and minor constituents and a few traces that happen to be free from a spectral interference. Over the years, there has always been a need for a fast qualitative and semi-quantitative analysis. This need even increased because of new legislation concerning toxic elements and waste disposal.

Also the complexity of new materials has caused tremendous problems to the wet-chemists and the cost of analysis is very high.

Now UniQuant offers new possibilities:

It can do a fast pre-analysis on all non-routine samples that are submitted to the lab. As many as 70 % may not need any further analysis. The pre-analysis is a great help in selecting the method for further analysis and for small samples it may be important that UniQuant has not in any way modified or polluted the samples so that they can subsequently be used for another method. A pre-analysis is also quite helpful in



conjunction with X-ray powder diffractometry. In conclusion, one may safely state that UniQuant will do away with a lot of the workload of wet-chemistry, AAS, ICP and EDX.

Typical UniQuant results

CDA 922 (Copper Alloy)

Element	Certificate	UniQuant
Cu	87.9	86.1
Pb	1.23	1.6
Sn	5.7	6.0
Zn	4.29	4.7
Mn	<0.005	<
Al	<0.005	<
Fe	0.05	0.064
Ni	0.66	0.82
P	0.032	0.026
As	0.012	<
Si	<0.005	<
Sb	0.07	0.065
S	0.035	0.088

RENE 41 (Nickel Alloy)

Element	Certificate	UniQuant
Ni	53.7	52.5
Cr	19.17	19.0
Mo	9.96	9.9
Co	10.59	11.0
Al	1.50	1.5
Ti	3.19	3.3
Cu	0.026	<
Fe	1.47	1.6
Si	0.07	0.041
Mn	0.02	<
P	0.004	<
S	<0.002	<
Nb	0.050	0.042
V	0.020	0.017

SS484 Tool Steel (Solid & Drillings)

Element	Certificate	UniQuant	
		Solid	Drillings
Si	0.20	0.18	0.13
P	0.030	0.033	0.015
S	0.024	0.025	0.079
V	0.94	0.90	0.86
Cr	5.17	5.5	5.5
Mn	0.21	0.23	0.23
Fe	(59.8)	59.9	60.4
Co	10.2	10.2	10.3
Mo	1.07	1.1	1.3
W	22.4	20.3	20.2

S1 (Basic Slag)

Compound	Certificate	UniQuant	
		Powder	Fusion
SiO2	19.4	20.9	17.2
Al2O3	3.1	3.3	2.2
FeO+Fe2O3	16.6+2.0	18.2	19.6
MnO	18.6	17.8	18.9
CaO	32.6	30.6	30.7
MgO	8.0	6.9	8.8
P2O5	0.47	0.44	0.44
V2O5	0.11	0.11	0.12
TiO2	0.53	0.51	0.49
Cr2O3	0.2	0.22	0.23
S	0.24	0.47	0.14
Na2O	0.1	<	0.28
K2O	0.10	0.08	0.09

N.B. Fusion is 15:1 Dilution

Nim G Granite (Majors)

Compound	Certificate	UniQuant
SiO2	75.7	74.5
Al2O3	12.08	11.6
Fe2O3	2.00	2.4
CaO	0.78	0.95
Na2O	3.36	3.7
K2O	4.99	5.7
F	0.42	(0.57)
MgO	(0.06)	0.06

Nim G Granite (Traces ppm)

Compound	Certificate	UniQuant
Ba	(120)	110
Ce	198	220
Mn	160	210
Nb	53	110
Pb	40	<
Rb	325	470
Th	52	<
Ti	540	980
Y	147	230
Zn	50	<
Zr	300	540

Environmental Sample

Compound	Certificate	UniQuant
Fe	1.20	1.25
Zn	0.12	0.055
Pb	0.14	0.10
Cu	0.018	0.008
Cr	0.05	0.075
Ni	0.017	0.013
SiO2	?	19.4
Al2O3	?	2.9
CaO	?	5.8
MgO	?	1.1
Na2O	?	1.8

Rest C,H,N Calculated by UniQuant = 64.3 %
N.B. Benefits of Matrix Identification

Polypropylene (ppm Levels)

Element	Certificate	UniQuant
Al	160	180
Si	480	390
Cl	55	87
Ca	140	150
Ti	49	56

Rest C,H,N Calculated by UniQuant = 99.83 %

Typical UniQuant 4 Results

Hast X (Nickel Alloy)

Element	Certificate	UniQuant4
Ni	47.5	48.07
Cr	21.9	21.61
Fe	18.35	18.39
Mo	8.6	8.29
Co	1.53	1.53
Mn	0.63	0.6
Si	0.52	0.56
W	0.46	0.39
Cu	0.12	0.15
Al	0.11	0.12
Nb	0.1	0.09
V	0.08	0.08
P	0.017	0.02
Ti	0.011	0.01

Steel A286

Element	Certificate	UniQuant4
Fe	56.4	55.89
Ni	24.96	25.14
Cr	14.06	14.18
Ti	2.15	2.25
Mo	1.08	1.03
V	0.26	0.264
Nb	0.23	0.231
Co	0.23	0.221
Al	0.19	0.186
Si	0.17	0.145
Mn	0.13	0.115
Cu	0.08	0.087
P	0.011	0.014
S	0.005	0.012

Cement NIST 1885

Compound	Certificate	UniQuant4
CaO	62.14	62.18
SiO2	21.24	20.83
Fe2O3	4.40	4.33
MgO	4.02	4.08
Al2O3	3.68	3.64
SO3	2.22	2.92
K2O	0.83	0.91
Na2O	0.38	0.58
TiO2	0.20	0.2
SrO	0.037	0.032
P2O5	0.1	0.087
Mn2O3	0.12	0.12
F	(0.05)	---
Cl	(0.02)	0.027
ZnO	(0.03)	0.025

Flint Clay NIST 97b

Element	Certificate	UniQuant4
Si	19.81	20.06
Al	20.76	20.72
Ti	1.43	1.36
Fe	0.831	0.763
K	0.513	0.55
Mg	0.113	0.105
Ca	0.0249	0.049
Zr	(0.05)	0.048
Na	0.0492	0.046
P	(0.02)	0.025
V	?	0.027
S	?	0.045
Cr	0.0227	0.021
Sr	0.0084	0.0076
Zn	(0.0087)	0.0071
Mn	0.0047	0.0039

Manual Input : LoI = 13.3 %

UniQuant Results on Small and Irregular Samples

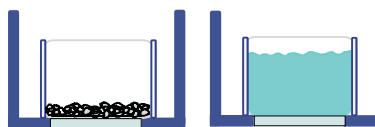
25.8 mg BCS 380 Aluminium Alloy			100.3 mg BCS 364 Leaded Bronze		
Element	Cert. %	UQ %	Element	Cert. %	UQ %
Al	94.61	93.3	Ca	78.6	80.6
Si	2	2.64	Sn	9.3	7.8
Fe	1.15	1.18	Pb	9.2	11.4
Ni	0.91	0.94	Ni	0.28	0.33
Cu	0.9	0.83	Sb	0.18	0.16
Ti	0.22	0.28	Zn	0.13	0.118
Mg	0.18	0.08			

Irregular Shaped Small Samples



Polypropylene
Insert to locate sample

Other Sample Types



Loose Powders
or Drilling

Liquids

UniQuant Typical Results

Drillings			Lube Oil		
Element	Cert. %	UQ %	Element	Cert. %	UQ %
i	0.2	0.13	Ca	0.12	0.15
	0.94	0.86	Mg	0.10	0.13
r	5.17	5.5	Zn	0.142	0.14
n	0.21	0.23	P	0.125	0.13
e	(59.7)	60.4	S	0.63	0.65
o	10.2	10.3			
o	1.07	1.3			
w	22.4	20.2			

The rest 98.74 (C + H + N) is calculated by UniQuant
UniQuant is used when no specific standards are available