UniQuant®5

Major features and benefits

Quantitative analysis of up to 79 elements
with reporting of practical confidence intervals ■

Standardless mode
for research and trouble shooting ■

Extended Fundamental Parameters (X-FP)
for versatility and full concentration ranges ■

Line overlap corrections using X-FP
for reliable minor and trace analysis ■

Variable sample mass
for very thin up to thick samples ■

Variable dilution
for use of catch weights ■

Determination of LOI or GOI
in case of bead analysis ■

Parent-Daughter principle
for fast accurate calibrations ■

Use of templates
for minimal routine data entries ■

User defined compounds
in addition to oxides ■

## a unique concept in XRF analysis

X-ray pioneer

In 1967, Willy de Jongh developed an innovative mathematical model for use in XRF analytical equations. For the first time it became possible to make highly accurate calibrations with significantly fewer reference standards than had previously been required and calibrations could be extended to cover much broader concentration ranges.

The equations contained interelement coefficients, called Alphas, which were calculated from theory making use of Fundamental Parameters.

Once calculated, these Alphas could be transferred from one instrument to another. X-Ray spectrometer users were thus able to solve the problem of interelement effects using so called 'theoretical' Alphas. At the same time, he was first (1967) to use regression analysis, as well as weighting of errors. It was the initial step along the road to today's 'standardless' analysis.

The de Jongh (DJ) model gained widespread use, with a number of subsequent mathematical models following similar principles. The method resulted in calibrations for very broad concentration ranges, however separate calibrations were still required for different types of samples.
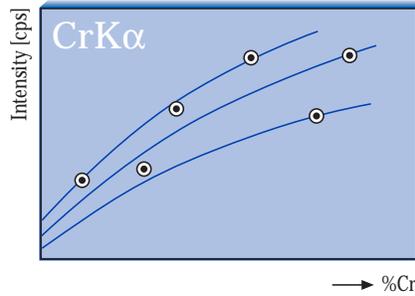
Calibration curves in the early XRF years.
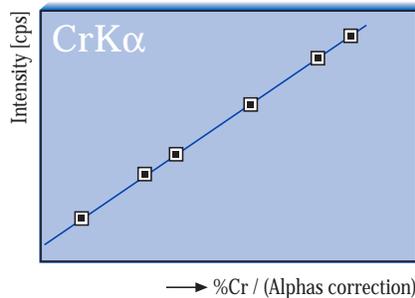
A calibration curve using alphas.
(Ref: W.K. de Jongh, X-Ray Spectrometry 2, 1973)
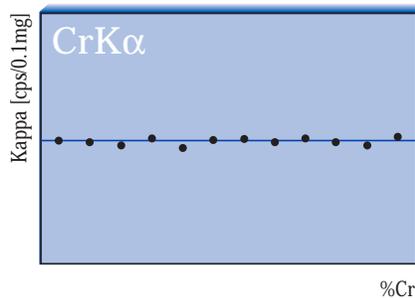
'Regression' in the 1990's using an average value obtained from any standards (UniQuant's Kappas). The calibration 'curve' is now a simple horizontal line allowing an arbitrary scale of the wt% axis.

New venture

In 1989, he established his own company under the name Omega Data Systems and started work on a new concept with the aim of using a single calibration applicable to all materials (e.g. alloys, glass beads, oil, polymers etc).

One of his new concepts involved the determination of instrumental sensitivities, designated Kappa's, which were totally independent of the analysed sample in having the dimension of cps/0.1mg. This enabled a single calibration to be applied to any sample matrix and resulted in the first version of UniQuant software.

UniQuant 1 was the first program for genuine standardless analysis, genuine because it worked without a library of standards. It provided quantitative analysis for up to 53 elements in virtually any unknown material, following an initial spectrometer calibration involving the measurement of a series of setting-up samples supplied as part of the package.

Constantly moving ahead

UniQuant 2 followed in 1992 - with further refinement bringing faster operation, a range increased to 77 elements and numerous improvements in user convenience.

Introduced in 1995, UniQuant 3 featured an extended fundamental parameter (X-FP) method to improve accuracy's for both major and minor concentrations. Spectral line overlaps are also treated by X-FP and are solved simultaneously with the concentrations. The extended FP method also accounts for variable sample thickness (mass/area).

In 1999, UniQuant 4 for Microsoft Windows® was introduced. A major improvement was interactive graphical support for intensities and the calculated backgrounds. This much facilitated trace analysis. See FIGURE 1 and 4a

The latest generation, UniQuant 5, launched in 2001 is a mature and user friendly package capable of answering an extremely wide variety of application needs.

UniQuant 5 for research and routine analysis

Since its introduction in 1989, UniQuant has continuously evolved. Traditionally, it provides good analytical accuracy's in its standardless mode that is based on sample independent calibration of spectrometer channels.

UniQuant is the only program that rigorously solves the problem of correction for more than 1500 potential spectral line overlaps and this by an extended form of the fundamental parameters (X-FP) method.

The X-FP method also enables to work with a variable sample mass (thickness).

To cope with heterogeneity effects such as encountered with mineral powder samples and many types of alloys, UniQuant 5 makes use of a new concept. A daughter calibration can be made very quickly by starting from a parent calibration and using one or a few standards.

Graphic supported weighted regression analysis is used for calibration with a suite of standards.

By UniQuant tradition, each reported calculated concentration is accompanied with an indication of a practical confidence interval, which is what makes UniQuant truly quantitative. In addition, theoretical standard deviations are given based on counting errors and propagation of such errors due to line overlaps.

Since data collection is peak based, the detection limits for trace elements are essentialy the same as with conventional methods. Accuracy's for minor and major elements over extremely wide concentration ranges are equal to or better than those obtained by conventional methods by virtue of using X-FP for matrix corrections.

UniQuant is outstanding in analyzing samples of any shape, size and physical nature as submitted to research labs, forensic labs or with trouble shooting in a processing plant. Now, UniQuant is also able to provide tailored multiple calibrations for highest possible accuracy's. In some cases, routine fusion of samples to a bead
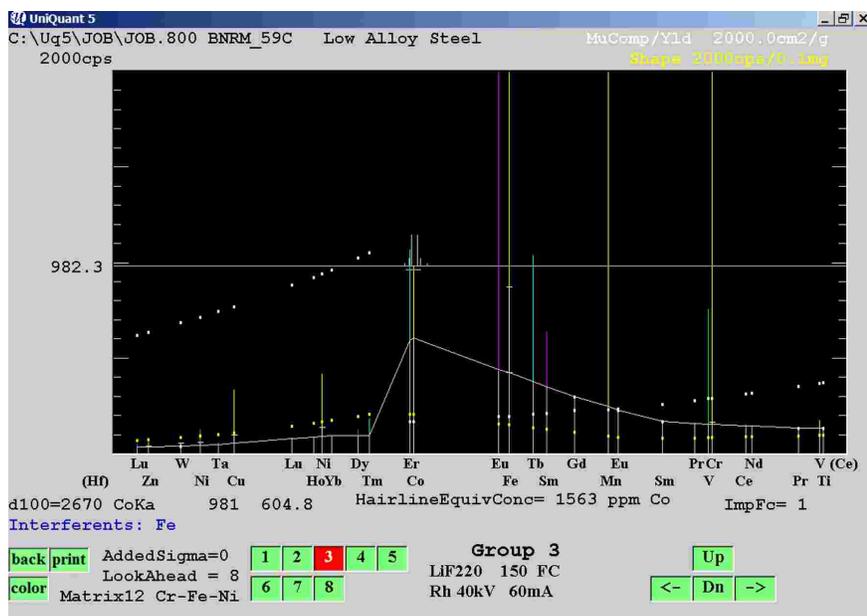

FIGURE 1. Reliable determination of trace elements supported by interactive graphical plots of intensities and concentrations

UniQuant® 5

can be replaced by a routine pressed pellet technique.

To minimize data entries in routine analysis, use can be made of templates, one for each application.

UniQuant 5 supports 79 elements, from Be to Am, including the Lanthanide elements. It distinguishes between Sulfur as sulfide and Sulfur as sulfate, and like wise for Phosphor.

As an addition to analyzing as oxides, UniQuant 5 introduces user defined compounds, such as sulfides, sulfates, fluorides and stearates. These are calculated stoichiometrically from one of the measured compound elements. If a compound contains more than one XRF feasible element or an element is measured by two XRF lines, the additional information may be used for a "second opinion" or for calculating a surplus as element or oxide.

Choose UniQuant 5 for...

- Research and Trouble Shooting
  - Quantitative analysis where no standards are available
  - Support for phase analysis by XRD
  - Analysis of small or odd shaped samples, or small amounts of powder samples
  - Determination of layer composition, mass/area and thickness
- Routine Analysis, Production Control
  - Quantitative analysis at highest accuracy by using standards
  - Using catch weights of sample and flux in case of beads, with automatic correction for variable dilution
  - Determination of LOI or GOI in case of bead analysis
  - Using catch weights of sample and flux in case of beads
  - Determination of S as sulfate and sulfide, P as phosphate and phosphide
  - Monolayer and aerosol samples, determination of mass and composition
  - Multilayer analysis, e.g. layers on steel or glass substrate
- Screening
  - Fast analysis of totally unknown samples
  - Determination of unexpected elements

The 115 XRF channels (79 elements) supported by UniQuant are calibrated for sensitivity and for spectral interferences by means of 64 samples, most of which are a single compound such as quartz and cryolite, or elements in the form of a metal foil. The 64 samples primarily serve to determine approximately 1500 line overlap coefficients.

In addition, they supply a "one point calibration" for each channel, one constant, Kappa, for each of the 115 Fundamental Parameter (FP) analytical (simultaneous) equations. These Kappa's can later be refined by using international and/or in-house standards. Only 11 of the 64 samples remain for use in maintenance, i.e. angle recalibration and monitoring of intensities.

Because Kappa's are independent of the chemical or physical nature of the material, UniQuant 5 is able to determine the composition of virtually any type of sample, including:

- Solid disks of metal or synthetic material
- Metal components, drillings, solid fragments
- Loose and pressed powders
- Painted or coated substrates
- Multilayer samples
- Solid solutions of minerals (glass beads)
- Lubricating oils and other liquids (from small drops to full sample cups)
- Deposited layers on filters
- Aerosols on filters

Example of the range of different samples which can be analyzed using UniQuant 5.

The Parent-Daughter principle

The Kappa's as obtained from one-point calibrations (see above) are generally used for analyzing totally unknown samples. They are contained in a Kappa List called "Any-Sample", that represents UniQuant's standardless mode. A new feature that has been introduced with UniQuant 5 is the use of multiple Kappa Lists, that is multiple calibrations.

Special calibrations are required for obtaining highest possible analytical accuracy's, for example in cases where heterogeneity effects are to be dealt with. Such effects do not only occur in mineral powder samples (mineralogical effects) but also in some types of alloys (metallurgical effects).

As opposed to conventional methods, it is not necessary to start from scratch when making a calibration for a new family of samples. Instead, use is made of an existing calibration (Kappa List), which is copied and named for example "Slag A". One, a few or a small suite of standards is then sufficient to tune the Kappa's such that they "absorb" heterogeneity effects. This tuning is generally, most important for major and minor elements, especially the light elements and is less or not important for many trace elements especially not when their radiation is at short enough wavelength. The resulting Kappa's in the daughter Kappa List deviate only slightly from those in the parent Kappa List. For analyzing an unknown sample, the appropriate Kappa List is selected from a list box, see FIGURE 2.

Use of templates

Each application consists of a measuring program and an associated evaluation program. Generally, both are tailored for a mininum number of channels and optimized measuring times for trace analysis.

To facilitate multiple applications and minimize data enties in routine analysis, use is made of "templates", one for each application. See FIGURE 2, commands T and G.

With each next analyte sample, a template can be selected from a list box, see FIGURE 2. The template is selected automatically in case of on-line operation, which is possible when the manufacturer's spectrometer software is supporting UniQuant on-line.
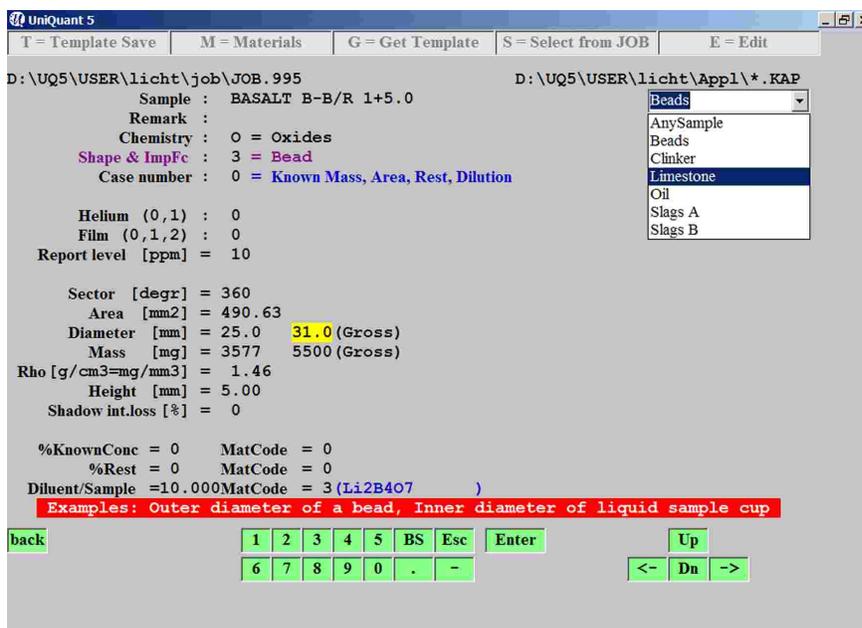

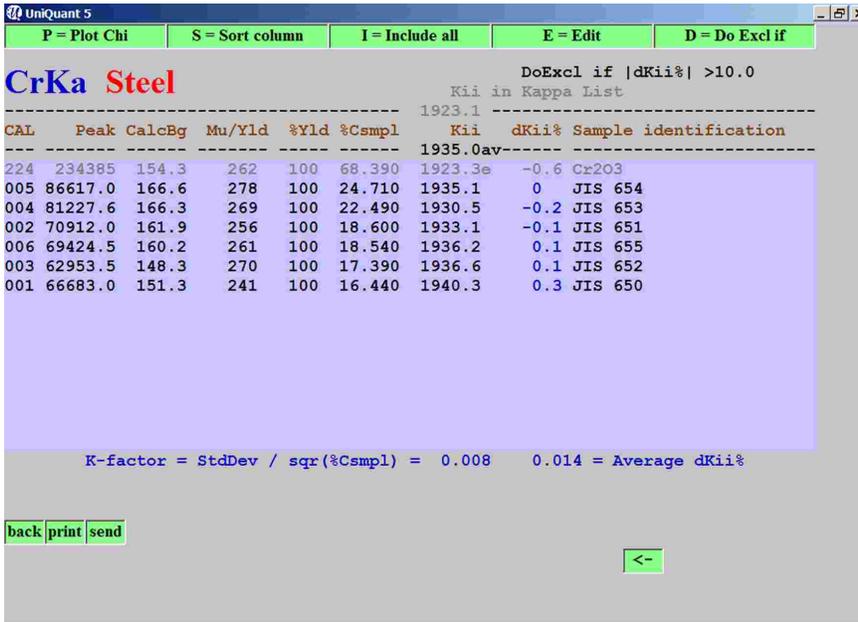*FIGURE 2. Selection of Kappa List from a combo box.*

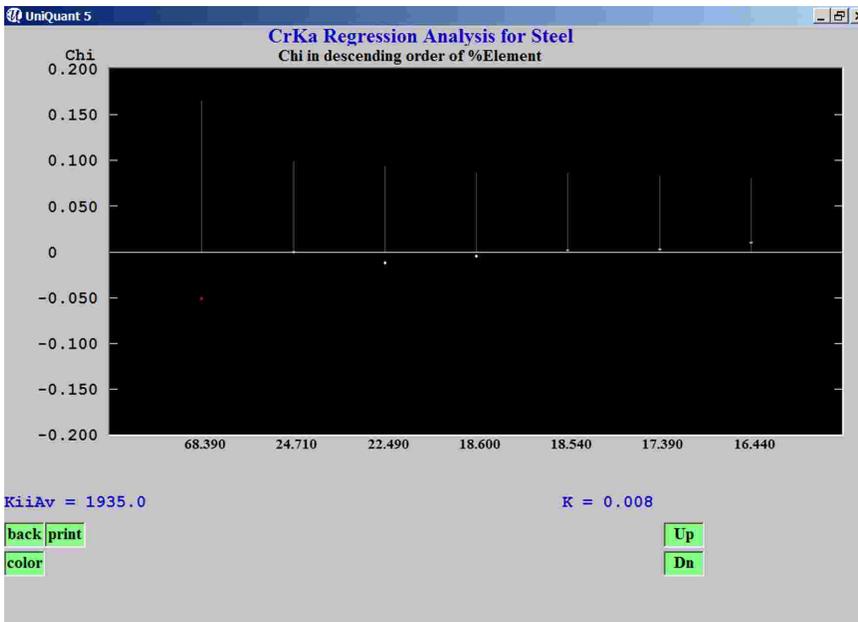FIGURE 3a. Refining Kappa for CrKα by regression analysis, in table form (above) and in graphical form (below).

FIGURE 3b. Deleting/including standards is by mouse operation.
K-factor= 0,008 indicates very high accuracy.

High accuracy

UniQuant 5 can easily be tailored for routine applications, such that analytical precision's, measuring times, detection limits and accuracy's are the same as with conventional XRF methods. UniQuant 5 has the additional advantage of being truly quantitative in that it reports theoretical and practical confidence intervals for each reported concentration. The practical confidence limit makes use amongst others of the K-factor found in weighted least squares calibration using at least two standards. The K-factor was introduced in XRF analysis by de Jongh in 1966. It reflects the accuracy for a wide concentration range rather than for just a particular concentration level. In fact

RMS [wt%] = Kfactor . $\sqrt{(\%C + \%Cb)}$, where Cb stands for equivalent background.

The K-factor is intended for concentration ranges above the equivalent background, that is not for trace analysis, for which RMS values are independent of concentrations. With high accuracy's, the K-factor is less than 0.020.

Regression analysis based on minimizing the K-factor

A refined calibration can be made for each analytical line. The example below is for a suite of 6 stainless steel standards. From each standard, a Kappa (Kii) has been found by measurement and

evaluation by Fundamental Parameters, see column Kii in FIGURE 3a. Their "weighted average" is shown at the top of this column. In fact, this calculation is the simpliest form of weighted regression analysis, since only one regression coefficient is to be calculated, Kii for CrKa in the example. It should be obvious that this requires only very few standards, two or a few more. This is in stark contrast with regression analysis in conventional methods, where many regression coefficients must be determined, these including line overlap coefficients, axis intercept, some infuence coefficients and possibly a few higher order influence coefficients. All these values are taken care of by UniQuant's fundamental parameters and unique separate determination of line overlap coefficients as well as of background.

FIGURE 3a shows a table of calibration standards used for the refinement of the Kappa, Kii, of CrKa. Deleting and including standards is by entering 'e' or space in a special column. Any change made gives instant recalculation.

FIGURE 3b The K-factor, here 0.008, is the weighted RMS of the plotted Chi values. A Chi value applies to an individual standard, whereas the K-factor applies to a suite of standards and a concentration range. Deleting and including standards is by mouse operation with immediate result. Deleted standards are shown as red dots.

Changes made in the table affect the graphical plot, and vice versa - the two are coupled.

In FIGURE 3c, all K-factors are well below 0.02. The RMS deviation for Cr and Ni at 25% levels is about 0.009 √25 or 0.05 weight%.

Interestingly, adding a 100% element sample as a standard to the set of standards (right columns), still gives good K-factors. This demonstrates that the Fundamental Parameter method provides accurate interelement corrections over extremely wide concentration ranges. A limiting factor is the possible occurence of metallurgical effects in certain ranges of elemental composition. In such case, a 'daughter' calibration can be quickly derived from a 'parent' calibration, see section 'the Parent-Daughter principle'.

The K-factors, found for the various XRF lines in a particular application, play a role in the calculation of practical confidence intervals, one for each concentration in an analyte sample.

When all constituents are measured, nor-malization to 100% improves overall analytical accuracy's. This is most beneficial for the elements at high concentrations and is at its best with concentrations that approach 100%. With analyte samples, whenever possible, UniQuant applies a weighted normalization to 100%. With normalization, the K-factor equation in a simplified form is:

$$\text{RMS [wt\%]} = \text{Kfactor} \cdot \sqrt{\{(\%C + \%Cb)\,(1 - \%C/100)\}}$$

K-factors with stainless steel standards JIS 650 to 651

```
    6 JIS standards              6 JIS + 100%sample

    Concentration                Concentration
    range in Wt%   Kfactor       range in Wt%    Kfactor

V    0.2  -  0.6   0.000          0.2  -  100    0.002
Cr  16    - 25     0.008         16    -  100    0.018
Mn   0.3  -  2     0.010          0.3  -  100    0.011
Fe  52    - 82     0.011         52    -  100    0.014
Co   0.04 -  0.4   0.016          0.04 -  100    0.036
Ni   0.2  - 20     0.009          0.2  -  100    0.025
Mo   0.01 -  2.5   0.016          0.01 -  100    0.016
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FIGURE 3c. Example of K-factors found from a suite of standards

Trace analysis

The analytical precision for trace elements is a function of intrumental parameters and measuring times and is essentially the same for the UniQuant method and conventional methods.

Analytical accuracy of trace elements also involves systematic errors, which may be due to errors in corrections for background continuum, spectral line overlaps and any spectral impurities. Each of these three corrections are made by UniQuant in a way that is very different from conventional methods, the latter mostly relying on regression analysis which in some cases requires a largely increased number of standards.

Background correction. With totally unknown analyte samples, there is not one single position in the entire spectrum for background measurement that is free from a potential line overlap. UniQuant succesfully addresses this problem without the need for searching a free position for background measurement.

Spectral line overlaps. UniQuant uses a unique concept in which line overlap coefficients are primarily a function of the selected instrumental parameters. Line overlaps by higher order reflection are automatically corrected for different absorption by means of Fundamental Parameters. There is no need to measure any interfering line itself, neither is
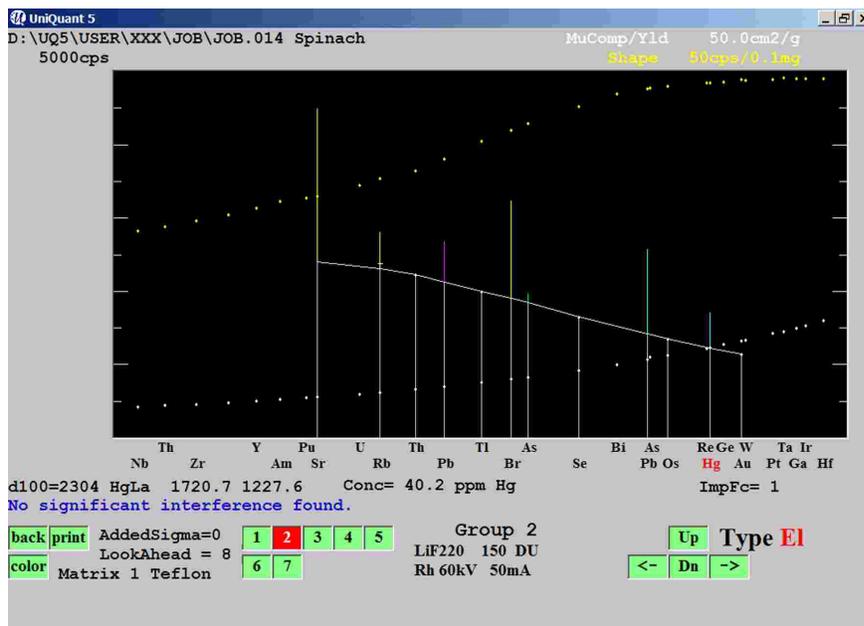
FIGURE 4a. Graphical plot of intensities

FIGURE 4b. Report to client

knowledge required of the scan profile of the interfering line. Without the UniQuant method, the determination of concentrations at trace levels in totally unknown samples can be unreliable or very cumbersome.

Spectral impurity factors are found from blanks in a special convenient calibration procedure. They are filed, one set of factors for various types of matrix, the default being teflon.

FIGURE 4a shows a graphical plot of intensities. Here the background continuum under the peaks are calculated from the channels ThLa, TlLb, SeKa, OsLb and AuLa. UniQuant uses these automatically by constructing the "under contour". For interpolations and extrapolations, use is made of a spectral shape (yellow points) and the absorption coefficients of the scattered radiation (white points). The application in the example was dedicated to plant materials. Only a sub set of 46 of 115 UniQuant XRF channels have been used, with ample measuring times for accurate analysis of 24 trace elements. If the analyst can safely assume that any of the elements Th Tl, Se, Os and Au (shown in the graph) will never occur at detectable levels, their channels can be declared to be the definite background channels. In special (rare) cases, special background channels can be inserted at user defined positions, as with conventional methods.

FIGURE 4b shows the calculated concentrations in the traditional UniQuant format, along with the practical "StdErr", the algorithm of which is described in the user manual.

Reporting

Several different types of reports are produced:

Report to client, FIGURE 4b, appears as a single-sheet printout per sample, destined for the analyst's client. Element or compound data are presented in the order of atomic number order and concentrations are reported with practical confidence interval, see column ('StdErr').

Simple report to client lists elements (and when applicable also as oxides or as user defined compounds) in descending order of concentration, or in alphabetical order of element names, again accompanied by practical confidence intervals. See FIGURE 5.

Combined table of results collects the results for a suite of samples into one common table, which can be laid out in various formats.

Report for the analyst shows the calculated concentrations in % or ppm, the counting statistical precision, the "equivalent" background that has been subtracted, and all corrections made for spectral line overlaps for a given sample. This comprehensive account is an invaluable tool for the analyst when assessing results.

In each case, the results are automatically saved as well formatted readable text. This enables easy visual check of data integrity and picking up results by LIMS programmers. Results can be printed or saved on the local hard disk or a remote hard disk.

C:\Uq5\JOB\JOB.811 NBS_620

Oxide	Mass%	StdErr	El	Mass%	StdErr
SiO2	73.60	0.13	Si	34.41	0.06
Na2O	12.54	0.05	Na	9.31	0.03
CaO	7.17	0.13	Ca	5.13	0.10
MgO	3.77	0.08	Mg	2.27	0.05
Al2O3	1.95	0.05	Al	1.03	0.03
K2O	0.368	0.006	K	0.306	0.005
SO3	0.260	0.015	Sx	0.104	0.006
As2O3	0.0700	0.0016	As	0.0530	0.0012
Fe2O3	0.0393	0.0012	Fe	0.0275	0.0008
SrO	0.0321	0.0028	Sr	0.0271	0.0024
ZrO2	0.0297	0.0028	Zr	0.0220	0.0021
TiO2	0.0162	0.0011	Ti	0.0097	0.0007

FIGURE 5. Simple report to client

UniQuant 5, so easy to use

UniQuant 5 combines rapid data entry and high calculation speed with extensive opportunity for interactive control. The user interface is structured to allow keyboard or mouse operation with an absolute minimum of effort.

The program is entirely menu driven. It uses a hierarchical menu structure to avoid desorienting in complexity. All data entries are checked for integrity at time of entry. Keyboard keys that do not have a function in a particular situation are inactivated.

There is an extensive online user manual with hyper links to related subjects. In addition, each command button has an extensive description that pops up by a right-click at the button.

To save operator time, batch modes are provided for evaluation of a suite of samples as well as of various processes during calibration.

Ease of maintenance

UniQuant has a monitor program, a facility for accurate drift correction of all analytical XRF lines without the need to monitor all these many lines. The procedure takes less than 15 minutes and is used for example every monday morning. The procedure serves UniQuant's standardless mode as well all dedicated calibrations. After a change of X-ray tube, it usually suffices to just run the monitor program.

Additional features and benefits:

- 79 elements from Beryllium to Uranium, including the lanthanides
- 79 primary XRF lines plus 37 alternative XRF lines
- A single monitor program to ensure stability for all calibrated programs
- Graphics support, also for Kappa's versus wavelength (XRF line), see FIGURE 6.
- Upward compatibility with previous versions
- Operation by mouse as well via keyboard
- Text in English, Japanese, German, Spanish or French
- Window can be sized up to full screen. For example, using half screen enables to run (start up) UniQuant more than once and yet see complete windows side by side.
- On line switching between two different color modes
- Immediate on line help for each command button
- On line manual with hypertext, links and index for installation, analysis of unknown samples and maintenance
- User specific data are all contained in one folder. This enables easy data exchange by e-mail in case of application support or intracompany data exchange.
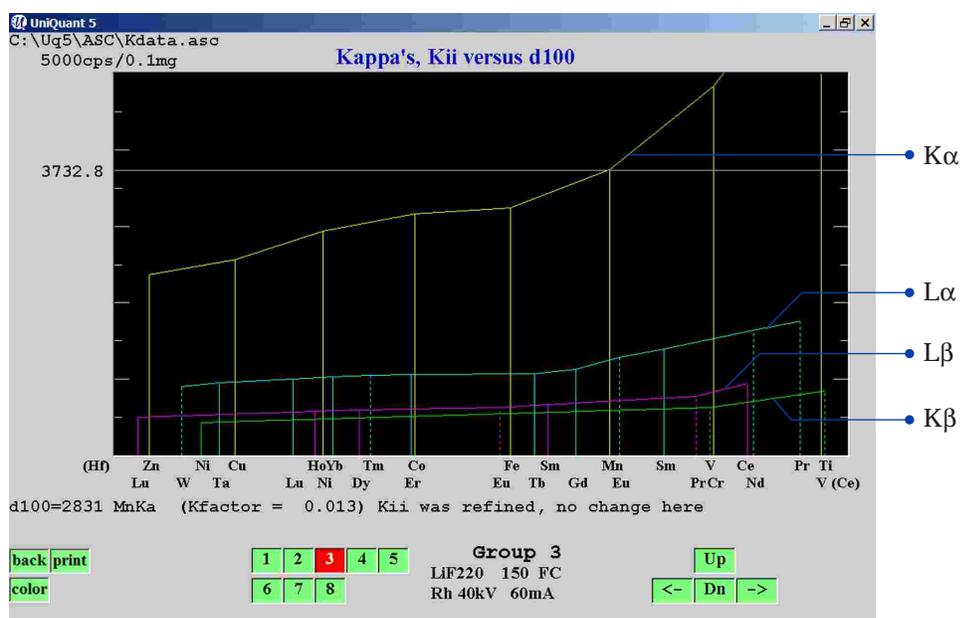- Tube filter, per group of XRF lines, can be specified by user

FIGURE 6. Plot shows consistency of spectrometer sensitivities. Kappa's of XRF lines for which no reference sample are available can be interpolated by mouse operation.

UniQuant® 5

Let's compare...

Peak-based versus Scan-based

Ever since WD-XRF spectrometers were introduced in the fifties, for quantitative analysis, intensities have been measured at fixed spectral positions. XRF lines are measured at their peaks whilst backgrounds are measured at interference-free off-peak positions. The latter can usually be pre-determined because each application is dedicated to a particular family of samples with a known set of elements, usually 10 to 35 elements.

In the late nineties, methods were introduced for analyzing totally unknown samples in which any of 79 elements may be present at a detectable level. One of the problems that had to be solved was that of background measurements, as this was not anymore a matter of measuring at pre-defined off-peak positions. With totally unknown samples, there is not even a single spectral position that is not potentially interfered by one or more XRF lines. In addition to the lack of pre-definable background positions, there is the huge problem of potential spectral interferences (line overlaps) of the analyte XRF lines themselves. Depending on selected spectral resolution, the total number of potential line overlaps is 1500 to 3000.

We saw two directions of development. All newly developed programs, except one, were based on fine step scanning of the entire spectrum. They are scan-based as opposed to peak-based. The exception was the UniQuant program that prescribes intensity measurements at up to 115 predefined spectral positions, all being analytical XRF line positions. UniQuant is peak-based as are all conventional quantitative WD-XRF programs.

At first sight, scanning of the entire spectrum is the most obvious approach since one would expect it to solve the problems of background and line overlap corrections with totally unknown samples. In reality, the scanning method poses its own set of problems. The most obvious one is that times spent at the analyte XRF lines are so short that elements may remain undetected when their concentration is less than 50 ppm. Lower limits of detection and determination are an order of magnitude larger than with measurements at fixed positions. Line overlap corrections are not as straight forward as one would expect. None of the scan based methods solves the problems rigorously and trace analysis is often unreliable.

To partially solve the trace analysis problem, some programs had later added the facility of measuring trace elements at their peak positions, a kind of hybrid solution. However, this does not work well with totally unknown samples, since the analyst does not know which trace elements are present or absent to start with.

Comparison of peak-based methods

From the start in 1989, UniQuant used several entirely new concepts. These addressed the problem of background measurements and line overlap corrections without the need of time consuming scanning. In the years that followed, the algorithms have been so much improved that trace analysis is now of the same quality as with conventional methods, the difference being that with UniQuant, unexpected trace elements are also determined in totally unknown samples. UniQuant calculates the background continuum taking into account any jumps that are due to absorption edges. Reliable and accurate trace analysis is a big challenge in X-ray spectrometry, if not the biggest. Sometimes, the best algorithms cannot compete with visual inspection. For this reason, UniQuant 5 offers full support by graphics, which is useful for critical trace analysis when setting up dedicated applications. Graphics also includes a breakdown of the gross peak of each analyte line into continuum, spectral impurity, line overlaps and net peak, all expressed in ppm, which is far more appealing than expression in cps.

Peak-based programs do not only differ in handling trace elements. There are also differences in the method of calculation of concentrations and in flexibility, such as for dealing with non infinitely thick samples down to thin layers, see Table of Comparison.

Table of Comparison

	UniQuant® 5	Conventional programs
Standardless mode included (for up to 79 elements)	✓	
Regression analysis when using standards	✓	✓
Few standards are sufficient in all cases	✓	
Good quality of trace analysis	✓	✓
Trace analysis with totally unknown samples	✓	
Line overlap corrections All 1200+ line overlap coefficients are pre-calibrated for use in any application	✓	
Passes 'acid test' of many mutual line overlaps with mixture of lanthanide elements	✓	
Interelement corrections by using *X-FP = Extended form of Fundamental Parameters* *MM = Mathematical models, using first and higher interelement correction coefficients*	X-FP	MM
Need for a theoretical alphas program for setting up a new application (calibration)		✓
Mass (thickness) of samples may vary (beads and light matrix samples are not 'infinitely thick' for many XRF lines)	✓	
Variable (catch) weights for sample and flux	✓	✓
Variable (catch) weight for liquid samples	✓	
Determination of LOI or GOI (Loss or Gain on Ignitions with beads)	✓	✓
Determination of mass/area (thickness) and composition of mono-layer, possibly on a fluorescent substrate.	✓	
Each result is reported with a practical confidence interval	✓	
One single monitor program for drift correction serves all calibrated analytical programs	✓	
Determination of user defined compounds	✓	

UniQuant 5: the product

Purchasers of a licence for the use of UniQuant 5 receive:

- A CD-ROM containing the UniQuant 5 program, data files and an electronic user manual

- A printed user manual

- A user licence

- A software protection device

- A set of calibration samples for initial set-up and routine maintenance

- Hardware accessories, such as sample masks and centring rings to facilitate the presentation of a wide variety of samples

Requirements to run UniQuant®5:

- Windows®95/98/ME/XP or Windows®NT/2000

- PC with Pentium processor

- Hard disk with free space of 10 MB for use by UniQuant

- CD-ROM drive

- Monitor resolution 1024x768 pixels (or more) for best results

Updates

UniQuant 5 licensees can download latest updates from http://www.uniquant.com

Data are subject to alteration without notice

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