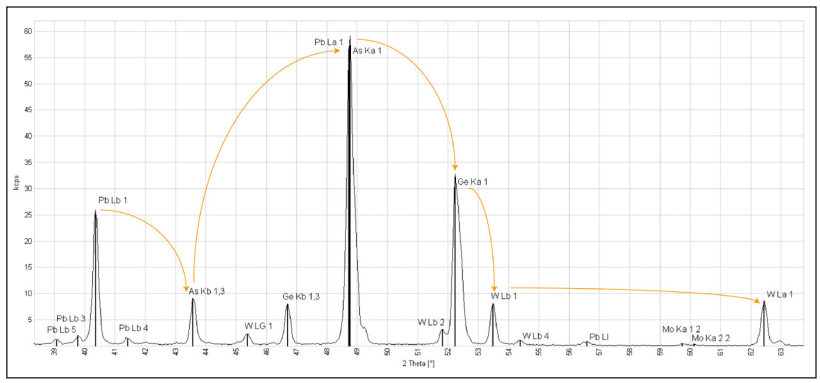
Thermo Scientific UniQuant

Program for quantitative XRF analysis using Thermo Scientific ARL WDXRF Spectrometers

UniQuant is a complete analysis package for standardless semi-quantitative to quantitative XRF analysis using intensities measured by a sequential X-Ray spectrometer. It represents a unique method in XRF analysis.



UniQuant uses peak by peak acquisition allowing for best limits of detection

Introduction to UniQuant

The program is highly effective for analyzing samples for which no standards are available. As its name suggests, UniQuant unifies all types of samples into one and the same analytical method. It is unique in that respect. Sample preparation is usually minimal or not required at all. Samples may be of very different nature, sizes and shapes. Elements from F up to Am (or their oxide compounds) are analyzed 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 goniometer. The reporting is in weight % along with an estimated error for each element.

UniQuant was first introduced as offline application software.

At that time, the program was for 53 elements and gave semi-quantitative to quantitative results. This first release of UniQuant was followed by four other major releases over the last 20 years, each of them introducing new advanced features such as increasing the numbers of elements that can be measured, better background calculations and introducing new refined calibration methods.

In 2013, the UniQuant application is completely redesigned and is now integrated within OXSAS as an option and is available for Thermo Fisher Scientific XRF sequential instruments. Existing instruments that are still using UniQuant 5 can be upgraded to the latest OXSAS version with integrated UniQuant.

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).

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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, Sulfides, 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.

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 also include those errors 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.

XRF spectrometer + UniQuant, an overview

For totally unknown samples, UniQuant needs 122 intensities as measured by 122 channels with instrumental parameters prescribed by UniQuant and stored in a standard OXSAS method. These parameters are kV, mA, tube filter, internal aperture, collimators, detectors and settings of the Pulse Height Discriminator.

For each unknown sample, the user must specify the so called "General Data" of the sample at analysis time or later. 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.

Why use UniQuant?

UniQuant can do a fast preanalysis on all non-routine samples that are submitted to the lab. Many of them 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. So UniQuant will do away with a lot of the workload of wet-chemistry, AAS, ICP and EDX.

In general terms, UniQuant provides:

- A quantitative analysis, if no standards are available, for up to 79 elements
- A quantitative analysis with highest accuracy if standards are available
- Determination of the % sulphur present as sulfide (reported as % S) and the % sulphur present as sulfate (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
- Screening samples and detection of unexpected 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

Table 1. Elements Analyzed

H																	*He*
Li	**Be**											**B**	**C**	**N**	**O**	**F**	*Ne*
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**	*Kr*
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	*Tc*	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**	*Xe*
Cs	**Ba**	***L***	**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	*Po*	*At*	*Rn*
Fr	*Ra*	***A***															

L	**La**	**Ce**	**Pr**	**Nd**	*Pm*	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
A	*Ac*	**Th**	*Pa*	**U**	*Np*	**Pu**	**Am**	*Cm*	*Bk*	*Cf*	*Es*	*Fm*	*Md*	*No*	*Lr*

Bold = Analyzed Elements / *Italic* = not known by UniQuant

About 50% of the current UniQuant users (more than 1000) only use UniQuant and no longer use conventional XRF analysis (calibration by regression). Part of them has 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 fine tune the UniQuant calibration and ensure the best quality for specific families of samples.

Major features

- UniQuant is calibrated as standard for the analysis of 76 elements (F to Am).
- A new calibration (daughter calibration) can 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 using only a few international or in-house standards
- All calibrations are maintained over time by the SUS program by means of intensity correction directly after measurements. This program is based on 'pure' metal samples, very stable, almost indestructible and easy to clean. One can compare the intensities from new measured samples with those measured years ago. This maintenance feature is unique and a huge time saver.
- 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
- 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. 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 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 (122 spectral positions) for determination of 76 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 that 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 favorable physical conditions. As a rule of thumb, the standard error in weight % for a major or minor constituent is equal to

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

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!

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 client's 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 and limits of detection

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 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. Thanks to peak by peak acquisition the counting time per element is much longer than in the case of a scan (40 to 100 times longer). This provides the best possible limits of detection.

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.

Thanks to the counting times used, spinning of the sample during analysis can be activated to even out inhomogeneities of the sample like grinding grooves on metals.

Interactivity

UniQuant has been designed for a maximum of interactivity. A pre-condition is speed of calculation. The user interface has been designed for a 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 sulfur.

The analyst concludes that the sample is a sulfide ore. This means that elements like Pb, Zn, Fe, Mo are as sulfide 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 Sulfides in the input of the General Data table and starts a second calculation. All this is a matter of a few seconds only.

On the other hand, UniQuant can be used on routine unknown samples that do not require advanced treatment by analyst. Once the analyst has refined the proper calculation for a given sample type, measurement of other samples of the same type can be easily taken over by any operator.

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 will take their effect into account.

Calculation of multiple samples

In order to short-cut a lot of work in case of multiple samples, a batch mode exists. Samples are "tagged" in a list and the "process" is started. It may be used for evaluating a suite of similar unknown samples or calibration samples as well.

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 various formats like DOC, XLS or PDF or re-directed to a specified file on disk.

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.

UniQuant as an OXSAS option

The UniQuant option includes:

- A licence for the use of the UniQuant option within OXSAS
- 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 10 calibration samples for initial setting-up and for maintenance
- Some small hardware, such as centering rings, to facilitate sample presentation
- On option, a set of 53 pure element samples is available. The total set of samples are used for factory calibration of UniQuant.

UniQuant is calibrated at the factory for elements fluorine (Z=9) to americium (Z=95) on the goniometer of the ARL PERFORM'X Series, ARL 9900 Series or ARL OPTIM'X 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.

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
SiO_2	19.4	20.9	17.2
Al_2O_3	3.1	3.3	2.2
$FeO+Fe_2O_3$	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
P_2O_5	0.47	0.44	0.44
V_2O_5	0.11	0.11	0.12
TiO_2	0.53	0.51	0.49
Cr_2O_3	0.2	0.22	0.23
S	0.24	0.47	0.14
Na_2O	0.1	<	0.28
K_2O	0.10	0.08	0.09

N.B. Fusion is 15:1 Dilution

Nim G Granite (Majors)

Compound	Certificate	UniQuant
SiO_2	75.7	74.5
Al_2O_3	12.08	11.6
Fe_2O_3	2.00	2.4
CaO	0.78	0.95
Na_2O	3.36	3.7
K_2O	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
SiO_2	N.A.	19.4
Al_2O_3	N.A.	2.9
CaO	N.A.	5.8
MgO	N.A.	1.1
Na_2O	N.A.	1.8

Rest C,H,N Calculated by UniQuant = 64.3%
N.A. = not available
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

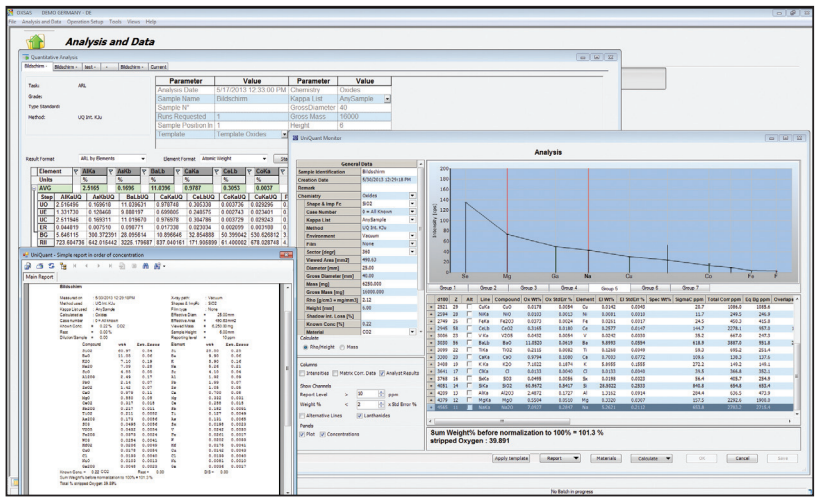
Rest C,H,N Calculated by UniQuant = 99.83%

Hast X (Nickel Alloy)

Element	Certificate	UniQuant
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	UniQuant
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



Both simple analysis results and advanced user screen are available to the analyst

Cement NIST 1885

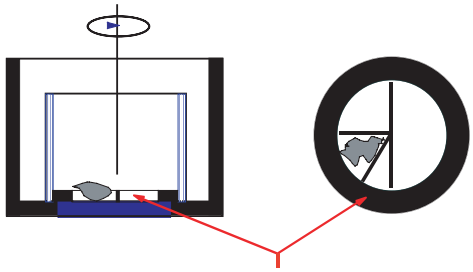
Compound	Certificate	UniQuant
CaO	62.14	62.18
SiO_2	21.24	20.83
Fe_2O_3	4.40	4.33
MgO	4.02	4.08
Al_2O_3	3.68	3.64
SO_3	2.22	2.92
K_2O	0.83	0.91
Na_2O	0.38	0.58
TiO_2	0.20	0.2
SrO	0.037	0.032
P_2O_5	0.1	0.087
Mn_2O_3	0.12	0.12
F	(0.05)	---
Cl	(0.02)	0.027
ZnO	(0.03)	0.025

Flint Clay NIST 97b

Element	Certificate	UniQuant
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	N.A.	0.027
S	N.A.	0.045
Cr	0.0227	0.021
Sr	0.0084	0.0076
Zn	(0.0087)	0.0071
Mn	0.0047	0.0039

Manual input: Lol = 13.3%
N.A. = not available

Irregular Shaped Small Samples



Polypropylene Insert to locate sample

UniQuant Results on Small and Irregular Samples

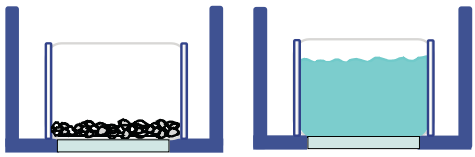
3 drillings: 25.8 mg
BCS 380 Aluminium Alloy

Element	Cert. %	UQ %
Al	94.61	93.3
Si	2	2.64
Fe	1.15	1.18
Ni	0.91	0.94
Cu	0.9	0.83
Ti	0.22	0.28
Mg	0.18	0.08

3 drillings: 100.3 mg
BCS 364 Leaded Bronze

Element	Cert. %	UQ %
Cu	78.6	80.6
Sn	9.3	7.8
Pb	9.2	11.4
Ni	0.28	0.33
Sb	0.18	0.16
Zn	0.13	0.118

Other Sample Types



Loose Powders or Drilling | **Liquids**

UniQuant Typical Results

Drillings

Element	Cert. %	UQ %
Si	0.2	0.13
V	0.94	0.86
Cr	5.17	5.5
Mn	0.21	0.23
Fe	(59.7)	60.4
Co	10.2	10.3
Mo	1.07	1.3
W	22.4	20.2

Lube Oil

Element	Cert. %	UQ %
Ca	0.12	0.15
Mg	0.10	0.13
Zn	0.142	0.14
P	0.125	0.13
S	0.63	0.65

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

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