

Elemental Analysis of Salt Rocks and Salt Solutions by the UniQuant X-Ray Fluorescence System

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ABSTRACT

A fast and reliable analyzing method for major, minor, and trace elements in salt rocks and salt solutions is offered by X-ray fluorescence (XRF) analysis. It is applicable to the special needs of geological and geochemical research as well as investigations on raw materials and products of the salt industry. Solid samples have to be ground to less than 50 µm grain size and pressed to a disk. Salt solutions are (after digestion) poured into a sample cup with a supporting film through which the solution is analyzed without the need for further sample preparation.

By using the UniQuant program instead of conventional computer programs, the need for elaborate sample-class specific calibration procedures is eliminated. The results are 'semi'-quantitative to quantitative from about 50 µg element/g sample (ppm) onwards. With additional care for the calibration, quantitative results can be achieved for all types of salt samples in about 20 min per sample. The comparison of our first XRF data from synthetic salt minerals, natural salt rocks, and salt solutions with results achieved by other methods, like atomic emission, titrimetry, and ion-chromatography, demonstrates the competitiveness of the X-ray fluorescence method.

INTRODUCTION

In geosciences and in the salt industry, chlorides and sulphates of the alkali and alkaline metals are still mostly analyzed by submitting a sample to several analytical methods. This requires the grinding of the rock sample and, after decomposing with acid or H₂O, a subsequent digestion as well as the filtration of non-soluble residues (e.g., clay minerals). Saturated salt solutions will have to be diluted by factors of 1-2·10⁵. This is particularly true if an analysis by ion chromatography (IC) is chosen (e.g., Herrmann et al. 1991).

The concentrations of Na, Mg, K, or Ca in different evaporite rocks may exceed 30% (mass fraction), while lower limits may be well below 1% (mass fraction). Differences in densities of the solutions for measurement as well as spectral line overlaps may disturb the determination of these elements by conventional methods like atomic absorption and emission spectrometry (AAS, AES) or flame photometry.

Methods like AAS, AES, and IC (ion Chromatography) as well as gravimetry and titrimetry are

usually expensive as they require a lot of time and manpower. Many investigations require extensive databases and thus large numbers of analyses, e.g. the research on underground repositories for hazardous wastes in rock salt (Knipping and Stier-Friedland, 1990; Herrmann and Knipping, 1993). The same is true for many applications of the salt industries.

Particularly in the last few years, XRF spectrometry established itself as a fast, reliable and economic method for multi-element analysis in earth sciences as well as in the chemical industry (basic principles of XRF are shown in Fig. 1; for further information see, e.g., Jenkins and de Vries, 1970; Bertin, 1970; Williams, 1987). Unfortunately, light elements like Na and Mg pose physical problems for XRF determinations. Thus evaporites and their secondary products, e.g. fertilizers, have been only scarcely analyzed by XRF spectrometry and with little success (e.g. Christensen 1985). Van den Enk et al. (1976) proposed the calculation of Na-concentrations using the anion-cation balance. This approach is often sufficient; but it is not applicable for

the examination of safety requirements, for instance with underground repositories for hazardous wastes in evaporite bodies.

Today, XRF-spectrometers include the necessary software for the calculation of spectral line coincidences and matrix effects (e.g., de Jongh, 1973). Nevertheless XRF measurements as a relative method are, at most, based on complicated calibrations via international certified reference material. Thus quantitative determinations are possible even for trace elements (between 0.1% and 1 $\mu\text{g/g}$). Depending on the number of elements to be analyzed and the respective calibration range, a larger amount of reference material is required. Again salt rocks and salt solutions pose additional problems as their main elements appear in large concentration ranges. Certified reference material does not yet exist for these samples. The production of these materials requires considerable expense because of the necessary statistical safety. In addition, solid and liquid samples require different measurement programs with special calibrations due to the sample matrices.

THE UNIQUANT METHOD OF STANDARDLESS XRF ANALYSIS

There has always been a need for a fast qualitative and 'semi'-quantitative analysis. This need increases with new legislation concerning toxic elements and waste disposal. The complexity of new materials (e.g., semiconductors) also causes additional problems for the analyst.

UniQuant is a PC program for semi-quantitative to quantitative XRF analysis using the intensities measured by a wavelength dispersive sequential X-ray spectrometer (Fig. 1). As its name suggests, it

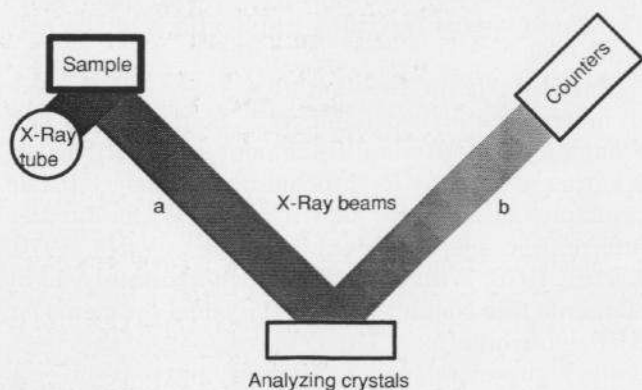


Fig. 1. Schematic X-ray path of a wavelength dispersive XRF spectrometer (simplified). a, polychromatic beam; b, monochromatic beam. The wavelength of b characterizes the atomic number (element), the intensity of b is proportional to the concentration of this element.

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			

Fig. 2. Periodic system of the elements. Elements which can be measured by the UniQuant XRF system are shown with dotted fields.

unifies all types of samples into one and the same analytical program. For the analysis of a sample, the method employed does not require any standards.

Elements from F up to U (or their oxide compounds) can be analyzed in such samples as a piece of glass, a screw, metal drillings, lubricating oil, loose fly ash powder, small pieces of PVC, phosphoric acid, thin layers on a substrate, soil, paint, and in general those samples for which no standards are available. An additional sample preparation increases the accuracy of the analysis.

Specially developed κ (kappa) equations are employed for UniQuant. Kappa's are intrinsic spectrometer sensitivities which are independent of samples. Inter-element corrections are made by means of so-called effective mass absorption coefficients, which have been calculated from fundamental parameters, including the primary X-ray spectrum (for further details see de Jongh, 1992, 1993).

The total analysis time is the same for all samples. After optimization for light elements it takes about 20 min for 62 elements (Fig. 2). If results are needed only for Na, Mg, K, Ca, Cl, and SO_4 , the measuring time can be reduced to less than 5 min per sample. The optimized configuration of the X-ray spectrometer of the Department of Salt Deposits and Underground-Repositories is as follows:

Spectrometer Type:	Philips PW1480
Generator:	100 kV
X-ray tube:	Rh anode, brass filter
Collimators:	300 and 700 μm
Analyzing crystals:	TIAP (carbon coated for better stability), Si111, LiF220
Miscellaneous:	Auxiliary collimator, 1 μm window at flow counter, Helium flushing

The accuracy for concentrations higher than 1% (mass fraction) primarily depends on the physical nature of the sample. The errors are smallest for

TABLE 1

Optimized measuring parameters for specific elements in natural salt rocks and salt solutions

	X-ray line	Analyzing crystal	PD limits	Line overlaps	Measuring time (s)	TLD ($\mu\text{g/g}$)	PLD ($\mu\text{g/g}$)
Bg	$\lambda = 1.355 \text{ nm}$	TlAp _{cc}	26-76		40		
Na	K α	TlAp _{cc}	27-77		60	20	40
Mg	K α	TlAp _{cc}	22-74	S	60	20	40
Bg	$\lambda = 0.850 \text{ nm}$	TlAp _{cc}	26-76		20		
S	K α	Si111	32-72		20	100	200
Cl	K α	Si111	32-72		20	50	100
Bg	$\lambda = 0.433 \text{ nm}$	Si111	36-66		20		
K	K α	Si111	36-68		10	10	20
Ca	K α	Si111	36-72		10	10	20
Fe	K α	Si111	36-68		6	100	150
Br	K α	LiF220	27-77		6	1	5
Rb	K α	LiF220	27-74	Br	6	1	5

Bg = background position; TlAp_{cc} = carbon coated for better stability; PD = Pulse height discriminator levels; TLD = theoretical limits of detection (bl = blank, s = standard deviation) = $\text{bl} + 3 \cdot \text{s}_{\text{bl}}$. PLD = practical limits of determination = $\text{bl} + 6 \cdot \text{s}_{\text{bl}}$ (rounded values).

thick full-area homogeneous samples (e.g., pressed pellets of fine-ground powder) and are quite acceptable for less favourable physical conditions (e.g., loose powders).

Generally, the results for trace elements in heavier matrices are reliable from 50 to 200 $\mu\text{g/g}$ onwards. In light matrices, determinations can be made from 5 to 10 $\mu\text{g/g}$ onwards (e.g., toxic elements in plastics, trace elements in oil, Br, Rb, and Sr in evaporites, see Table 1).

PREPARATION OF SOLID AND LIQUID SAMPLES

Salt minerals and rocks

Particularly with the XRF analysis of light elements such as Na and Mg, their long-wave, low energy fluorescence radiation ($\lambda_{\text{Na}} = 1.19 \text{ nm}$ and 0.99 nm respectively) is strongly absorbed within the sample. In principle, it is only the sample surface (the first 5–10 μm) that contributes to the intensity of the measured fluorescence intensity.

Thus a homogenous distribution of all constituents of a sample is necessary. For highest precision, glass fusion discs are required (e.g. Norrish and Hutton, 1969; Palme and Jagou, 1977; Eastell and Willis, 1989). 600 mg of the sample are thoroughly mixed with a suitable melting agent (e.g. 3600 mg of lithiumtetraborate, $\text{Li}_2\text{B}_4\text{O}_7$) and 1000 mg of NH_4NO_3 as an oxidizing aid. This mix is molten at 1100°C . After cooling the sample, a glass fusion disc

with a homogenous distribution of all elements (a 'solid solution') is obtained. There are neither problems with homogeneity nor with grain size effects which could falsify the measurement.

Except for pure NaCl (Halite), this preparation method is in our experience not applicable for other chlorides, e.g. $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$ (carnallite) or minerals such as $\text{KMgClSO}_4 \cdot 2.75\text{H}_2\text{O}$ (Kainite) because of the volatility of the Cl-component at high temperatures. Even with greatest care, the loss of Cl in glass fusion discs is not reproducible.

Another common preparation method is the use of pressed pellets (e.g. 40 mm \varnothing) of the ground and homogenized sample. The absorption of long-wave fluorescence radiation may nevertheless falsify the accuracy due to grain size effects (e.g., Nielson and Rogers, 1986). To minimize these effects, the samples have to be ground as finely as possible (<50 μm) and show an homogenous grain size distribution. To avoid coating effects, the selected pressure for making the pellets is an important variable.

To obtain small grain sizes and homogenous grain size distributions, several grinding methods have been tested. The commonly used laboratory planetary or disc mills are not applicable because of the hygroscopic character of several salt minerals (e.g. carnallite, sylvine). The sample powder coagulates and more coarse particles are protected from further disintegration. Inhomogeneous grain size distributions are the result (Fig. 3).

We achieved the most satisfying results (Fig. 3) with a so-called micronizing mill (McCrone, London,

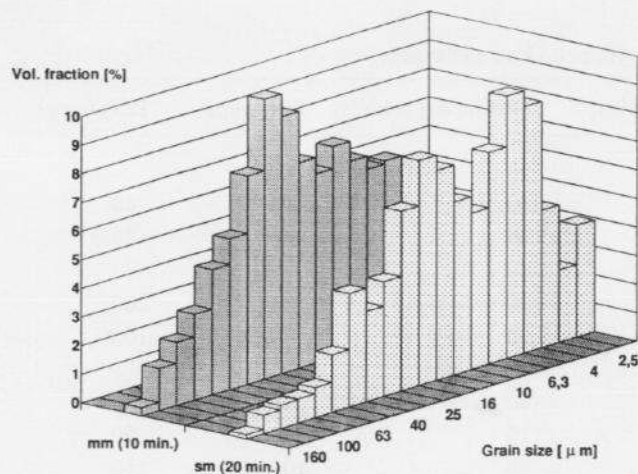


Fig. 3. Grain size distribution of a carnallite sample after grinding in a swing mill (sm; 20 min grinding time) and in the micronizing mill (mm; McCrone, London, UK; 10 min grinding time). The more homogeneous grain size distribution is obvious after using a micronizing mill.

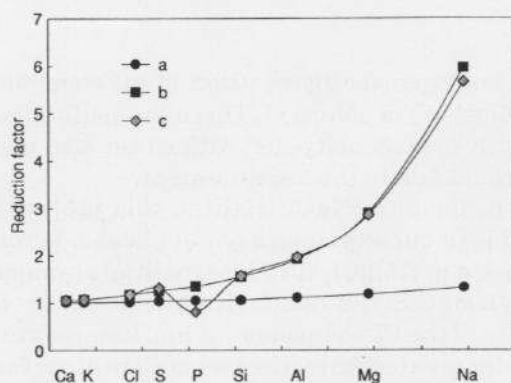


Fig. 4. Reduction of fluorescence intensities as a function of wavelength and the atomic number respectively. a, Helium; b, helium with polypropylene film; c, helium with Mylar film. Reduction factor = ratio measurement in vacuum without film/measurements in helium without and with films (jugs have been pre-stretched prior to their use; see text). The Mylar film is contaminated with P and Ca.

UK). The disadvantages of this mill type are the soft polypropylene jars and a time-consuming cleaning procedure. With an altered design, even samples with higher hardness, e.g. silicates could be ground satisfactorily.

The optimum conditions with maximum reproducibility and time were obtained with a 10 min grinding time of a 10 g sample (Knipping et al., 1992). Stable pellets result from a pressure of 8 kN for 8 s. The addition of suitable binding agents (e.g. Hoechst Wax C) in combination with Al-cups is only necessary with pure sulfates. In this case the respective dilution of the sample with 1000 mg of wax has

to be considered when defining the measuring parameters of UniQuant.

Saturated salt solutions

In respect to homogeneity, the XRF analysis of salt solutions poses no problems. In a similar way as for other determination methods, the sampling procedure of natural (and synthetic) solutions should avoid solid phases (Herrmann, 1980). If this is impossible, a subsequent filtration must be carried out. Saturated solutions should be diluted with demineralized water by factors of 1–10, because the sample will be heated to about 35°C during the measurement. This can lead to a slight evaporation of water and hence to crystallization of solid phases resulting in incorrect analytical results.

As the irradiation is usually done from underneath the sample (Fig. 1), liquid samples have to be measured in a plastic cup (e.g. polypropylene), with a bottom of stretched thin film. Apart from the commonly-used Mylar film (polyethyleneterphalate), polypropylene can be applied successfully. Unlike Mylar, the latter is almost free from such contaminants as P and Ca. In addition, long-wave fluorescence radiation (light elements such as Na, Mg etc.) will generally be absorbed, to a greater extent, by a 2.5 µm Mylar film in comparison to the mechanically more stable 6.3 µm thick polypropylene film (Fig. 4).

The mechanical stress on the film whilst stretching it onto a plastic sample cup may lead to non-reproducible changes in film thickness. This effect results in decreasing reproducibilities for the measurement of light elements. To overcome this problem we designed a simple tool to pre-stretch the sample cup and introduce the film with reproducible tension. This resulted in a stable system cup/film and improved reproducibilities of the analytical data.

MEASURING PARAMETERS

Table 1 shows the XRF measuring parameters for selected elements, including limits of detection and limits of determination in natural salt rocks and salt solutions.

Kocman (1989) observed a dehydration of gypsum samples during the measurement under high vacuum. Our investigations do not support this observation. Nevertheless, we measure all salt rock samples, such as all liquid samples, under a He atmosphere, because of water loss in samples containing carnallite and subsequent falsification of the analytical data (Knipping et al., 1992).

TABLE 2

Comparison of the first XRF results of synthetic KCl and NaCl and 2 salt rocks with values achieved with other methods

	KCl		NaCl		Ev-HK		Ev-HA		s_{rel} XRF (%) N = 25
	XRF	Other methods	XRF	Other methods	XRF	Other methods	XRF	Other methods	
Na	—	—	38.6	39.3	28.7	28.5	21.2	21.2	±0.09
Mg	—	—	—	—	2.5	2.4	0.8	0.3	±0.07
SO ₄	—	—	—	—	8.1	9.8	6.7	5.4	±0.17
Cl	47.2	47.2	61.2	60.7	50.1	49.7	48.6	50.1	±0.51
K	52.4	52.5	—	—	8.4	7.6	19.9	20.0	±0.15
Ca	—	—	—	—	0.4	0.4	2.7	1.9	±0.5
Br	—	—	—	—	360	350	1149	1250	±3
Rb	—	—	—	—	46	70	30	57	±5

Data for Na, Mg, SO₄, Cl, K, and Ca mass fraction in %, data for Fe, Br, Rb, and Sr in µg/g.Conventional methods = atomic absorption spectrometry: Ca, Mg; atomic emission spectrometry: Na, K, Rb; flame photometry: Na, Mg, K; titrimetry: Mg, Ca, Cl, Br; gravimetry: K, SO₄. s_{rel} = relative standard deviation, given for the specific concentration range.

N = number of preparations and analyses of one single sample.

REPRODUCIBILITY AND ACCURACY OF THE XRF RESULTS COMPARED WITH OTHER METHODS

As previously mentioned, there are no certified reference samples available to test analytical results of salt rock samples and similar material for reproducibility and accuracy. We therefore used synthetic minerals (suprapur reagents: NaCl, KCl) as well as In-House-Standards (TUC-EV-HK and TUC-EV-HA). Table 2 presents our first results.

In Table 3 and Fig. 5, the results of the XRF analysis of two natural salt solutions from a potash mine are compared with data achieved with other methods. It can be seen that there are only small differences between the results of the distinct analytical methods.

CONCLUSIONS

XRF together with UniQuant can do a fast pre-analysis of major and trace elements on solid and fluid samples that are submitted to the lab. The pre-analysis is a help in selecting the method for further analysis. For small amounts of 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 helpful in conjunction with X-ray powder diffractometry (Siemann, 1992).

Our investigations demonstrate that XRF spectrometry with UniQuant enables fast quantitative

analysis of salt rocks and salt solutions, following suitable sample preparation procedures and an optimization of parameters (background positions, X-ray line overlaps, measuring times).

It should be mentioned that our UniQuant installation has been optimized to the requirements for the elements described but is still universally applicable to all kinds of samples.

TABLE 3

Comparison of the first XRF results of two saturated salt solutions with values achieved with IC (ion chromatography)

	AB 1a		LG H		s_{rel} XRF (%) N = 25
	XRF	IC	XRF	IC	
Na	0.67	0.62	1.3	1.2	±4
Mg	6.8	6.8	6.2	6.0	±0.5
SO ₄	0.002	0.02	2.5	2.2	±0.5
Cl	22.5	22.3	19.8	19.6	±1
K	0.96	0.82	2.1	2.1	±2
Ca	0.27	0.30	0.009	0.005	±2
Fe	1300	n.m.	490	n.m.	±1
Br	2789	2847	1572	1530	±0.5
Rb	<ld	n.m.	160	n.m.	±0.5

Data for Na, Mg, SO₄, Cl, K, and Ca mass fraction in %, data for Fe, Br, and Rb in µg/g; <ld = < limit of determination; n.m. = cannot be measured with the used equipment. s_{rel} = relative standard deviation, given for the specific concentration range.

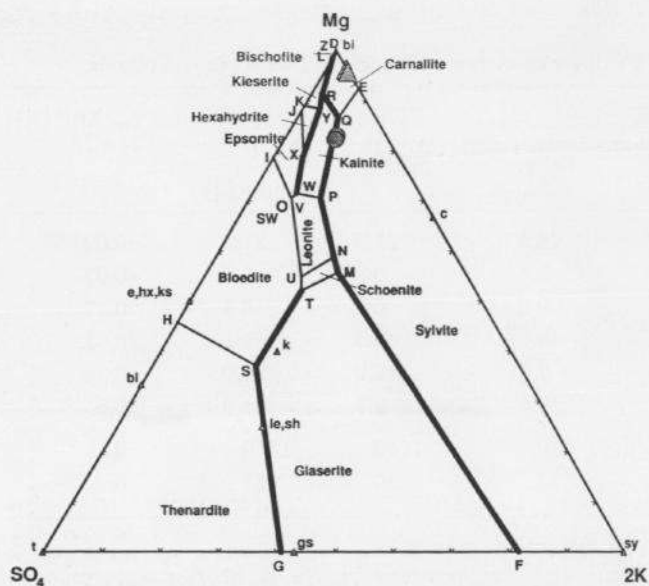


Fig. 5. Results of Table 3 plotted in the Quinary System of marine evaporites (at 25°C). Circles = sample LG H, triangles = sample AB 1a. There are obviously little differences between the analytical methods.

A future task for achieving more accurate quantitative results is further optimization, concerning line overlaps and background strategy. This will include elements like Si and Al, which are the main components of the non-soluble residues in salt rocks ('salt clays').

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