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ASSESSMENT OF QUANTITATIVE SALT ANALYSIS BY THE WATER EXTRACTION METHOD ON LIME MORTARS.

BLÄUER BÖHM, CHRISTINE

BCD GmbH, Wankdorffeldstr. 102, 3000 Bern 22, Switzerland

SUMMARY

Due to the lack of a practicable direct method, quantitative salt analysis of mortar samples is usually performed indirectly, by extracting the salts from the sample with deionized water, then analysing the relevant ions in solution and finally recalculating the ion concentration per gram sample. The exact procedure e.g. sample drying, ratio water to sample used for the water extraction, extracting time and temperature, methods for the wet chemical analyses etc., must be selected carefully to make sure, that all water-soluble salts present in the sample are actually brought into solution and subsequently analysed. Several analytical approaches are published in the literature. Out of these, our way of sample treatment and analysis was selected, aiming to preferably use simple technical equipment and to suit also situations with limited funds. In short the following procedure was selected: ratio water to sample = 100:1; extracting time = 2 minutes; measurements of pH and electrical conductivity; analyses of sodium by means of a sodium ion selective electrode; analysis of K^+ , Mg^{++} , Ca^{++} , NH_4^+ , Cl^- , NO_3^- and SO_4^{--} by means of filter photometry. This procedure was then tested on samples with known salt content. The analysing methods were additionally compared to flame photometer analyses and atomic absorption spectroscopy and ion chromatography.

The test showed that our analyses give a very good picture of the actual salt content within the samples and also the comparison of the different methods to measure the ion concentrations did correlate quite well. The detection limits of the used filter photometry tests for sulphate and to a lesser extent for potassium are however not very satisfactory. The measurement of the electrical conductivity revealed to be very important, as it gives a very good indication of the total ion content of a sample.

Estimation d'analyse quantitative par la méthode "extraction par de l'eau" appliqué aux mortiers a chaud.**RÉSUMÉ**

Il n'existe aucune méthode directe pour faire des analyses quantitatives de sels dans des mortier. Pour cette raison l'analyse est normalement exécutée en extrayant les sels de l'échantillon avec de l'eau déminéralisée, puis en y analysant les concentrations des ions déterminantes et en recalculant les concentrations par gramme d'échantillon. La procédure exacte, par exemple la façon de sécher, la quantité de l'eau à utiliser, la durée de l'extraction, les méthodes d'analyse des ions, etc. doivent être choisis soigneusement pour pouvoir être sûr que tous les sels solubles dans l'eau soient mesurés. Plusieurs approches pour ces analyses ont été publiées, dont nous avons choisi notre façon à faire ces analyses, en préférant les techniques simples et bon marchées. Brièvement la procédure suivante a été choisi: proportion entre eau à échantillon = 100:1; durée d'extraction = 2 minutes; mesures du pH et de la conductivité électrique; analyse du sodium avec la méthode d'électrode sélective; analyses des ions K^+ , Mg^{++} , Ca^{++} , NH_4^+ , Cl^- , NO_3^- et SO_4^{--} par tests de photométrie à filtre. Cette procédure a été testée sur des échantillons avec teneur connues en sels soluble. Les méthodes d'analyse ont aussi été comparées aux mesures par photométrie de flammes, spectroscopie d'absorption atomique et chromatographie d'ions.

Les tests ont montré que nos analyses donnent une image bonne du contenu en sel soluble dans les échantillons et que les résultats se situent dans la même ordre de grandeur que les résultats des autres méthodes d'analyse. Les limites de détection, en utilisant la photométrie à filtre, ne sont pas très satisfaisant pour les tests du sulfate et un peu moins de potassium. Les mesures de la conductivité électrique donnent une bonne idée du conteu total en sels.

1. INTRODUCTION

Within building materials salts are either present as individual salt phases or they are dissolved and therefore are contained as ions in the pore water solution. Theoretically crystalline salt could be analysed qualitatively and quantitatively by means of e.g. X-ray diffraction or infra red spectroscopy. In practise this is hardly ever possible, because of the elevated detection limits and because calibration curves for each individual salt would be needed for quantitative analysis. Direct analyses of the pore water {12} is usually not possible either, because of the huge sample size needed to gain only a little amount of pore solution, and the very sophisticated analytical instruments needed as well for the extraction as for the subsequent water analysis. Hence the easiest practicable and most frequently used method to analyse the salt content within building materials is to extract the salts by means of deionized water and analyse the ion content of the extracted solution.

The water extraction method can be used for mortar and stone samples, but as well to analyse any kind of poultice, that was used to extract salts from wall paintings or stone. This paper concentrates exclusively on the discussion of salt analysis of mortar and stone samples, as for poultices the sampling, the water extraction method, as well as the interpretation of the results are different.

Sampling in historical buildings is restricted to areas where no damage can be done to valuable historical substance, this means that the samples must be taken at places which are already damaged, or the samples come from repair materials, and the results have to be extrapolated to the original materials. Additionally the amount of sample that can be taken is usually rather restricted, this gives a certain limitation to the precision of the results. However when performing salt analysis the aim is usually to find out trends of salt distribution and orders of magnitude of salt content. We would like to answer questions like "is there more salt in one place than in the other, and if so, are the ratios of the individual ions the same in both places or to what extent do they differ?"; or "does this stone contain more salt than the same type of stone freshly quarried?"; or "is this building material a potential source for salts?" etc. To answer such questions it is not necessary to perform analysis that give results at [ppm] or even [ppb] accuracy, but the results must be coherent and relevant to the questions asked.

The methods for salt analysis and their interpretations discussed below, were developed and tested keeping all the restrictions in mind, that have to be faced, when the task is to analyse the salt system of a historical building. As the funds are very often limited as well, it was a further aim of the study to show, what the value of simple measurements can be, without becoming too simplifying.

2. SAMPLING AND SAMPLE PREPARATION

Depending on the questions to be answered sampling will be slightly different, nevertheless for each individual analysis at least 0.5g (better 1g) of sample is needed, if the analysis is performed the way it will be outlined below..

All sampling has of course to be done without using any water at all. For the evaluation of salt distribution profiles into the depth of a wall, cores may be drilled. These cores need to be brushed (dryly) to avoid contamination of the deeper sections by the drilling dust from the shallower sections, especially in very moist building materials. The drill cores are then cut in sections and each section is analysed separately. It is of course also possible to just using the cuttings from drilling.

Surface profiles can give the distribution of salts depending on the distance to their source (e.g. ground moisture, alkaline building material, etc.). Such samples should all be taken to the same depth to be comparable {8}. In locations with changing climatic conditions, the salt distribution will change with dry and wet climates, therefore all samples to be -compared should be taken at the same time. However, samples taken at different climatic conditions can of course give the fluctuation of the salt concentrations with climate.

For an evaluation of a salt distribution over a surface or a similar aim, it is necessary, that all samples have about the same chemical and mineralogical composition, apart from their salt content, and the same porosity,

because otherwise differences in salt content are maybe just due to differences in permeability of the material. All samples have to be crushed to about the same grain size. This can be important for samples containing minerals with a low solubility in water, e.g. for calcite (CaCO_3) the portion dissolving in water during the extraction procedure is double for samples crushed to powder compared to samples crushed to a larger grain size [3]. However such differences will only play a major role in samples containing little salt.

3. WATER EXTRACTION PROCEDURE

The sample is crushed (wrapped in clean paper) with a hammer to a maximum grain size of about 2 [mm] in diameter and then dried to constant mass [10] at 42 [°C] and subsequently conditioned to room climate (40% to 60% relative humidity, 20 to 25°C) over night

Samples that contain very hygroscopic salt mixtures can hardly be weighted accurately after drying in the oven, because they absorb water from the surrounding air so quickly, that they constantly gain weight on the balance. However the samples have to be dried previously to conditioning to room climate, because otherwise conditioning lasts much longer and from hysteresis of sorption and desorption isotherms we know, that the equilibrium moisture content at a certain relative humidity is lower for sorption, than for desorption. Sorption at relative humidities between 40% and 60% of inorganic building materials does not vary much with varying relative humidity, and stones that are strongly contaminated with hygroscopic salt mixtures do only show an enhanced water uptake at relative humidities above 70% (information kindly given by Steffen Laue).

1g (or 0,5g) of the sample are weighted and washed by means of deionized water into a measuring flask of 100ml (or 50ml) volume and the flask is filled to the filling mark with deionized water.

When preparing the water to sample mixture like this, the sample takes also a part of the filling volume of the flask. If the density of the mortar is estimated to be 2.5 [g/cm^3], the sample takes up 0.4 [%] of the filling volume. As the exact density of each sample however is not known, this value is ignored when calculating the salt content, and it is assumed that the ration sample to water is 1:100. We tried also to add the water by means of a pipette to the sample. This only works out well, if the sample can be weighted directly in the flask, because otherwise either some sample dust or water droplets remain uncontrollably but observably on the weighing container. Furthermore we found in our tests, that the final results did not differ in any way that could be related to the choice of this method.

Rösch & Schwarz [11] mix 1 gram of sample with 50 millilitres water, and hence produce a more concentrated salt solution. We found nevertheless in our analysis that with dilution 1:100 the resulting solution has, in most cases, a salt concentration, that allows to directly use ordinary water analysis tests, without needing to dilute and that even poorly soluble salts such as gypsum would go in solution with that procedure.

The sample and water mixture is shaken hard for about two minutes.

This follows the procedure of Zehnder [13], other authors choosed much longer extracting times ([7] 30 minutes; [11] 60 minutes-, [3] 90 minutes). Longer contact times lead to the partly dissolution of sparingly soluble constituents (e.g. Calcite, [13])

The suspension is then filtered with the aid of a water jet filter pump over a polyamide membrane filter of 0.45 [μm] pore size.

The residue is dried in the oven at 42°C to constant mass and the weight loss is calculated from the differences between the weights of the sample before and after the water extraction procedure.

The electrical conductivity and pH of the filtrate are measured immediately after the filtration. Then the filtrate is filled into polyethylene bottles and - if necessary - stored in the refrigerator. Subsequently the concentrations of the individual ions are analysed by water analysis methods.

4. METHODS OF WATER ANALYSIS

4.1 Limits of the analysis

The most abundantly found components of soluble salts from monuments are Na^+ , K^+ , Mg^{++} , Ca^{++} , NH_4^+ , Cl^- , NO_3^- , SO_4^{--} , CO_3^{--} , HCO_3^- and H_2O {1}. Although other ions, such as nickel {2}, lithium (e.g. from the use of lithium water glass), phosphates or oxalates {9}, to name only a few, can form soluble salts causing damage to building materials as well. Depending on the method used to analyse the water extract (see e.g. {6}), several of the above mentioned ions can be detected together in one analytical step and are therefore not accidentally missed out, however if the water extracts are analysed by ion selective tests, only the ion in consideration will be detected and the presence of other ions will not necessarily be recognised.

There exists no direct method to analyse carbonic acid or its anions {6}. Hydrogen carbonate or carbonate are measured titrimetrically in water analysis, but as these tests need a lot of testing water - usually no problem when analysing natural waters - they cannot normally be performed with water extraction samples, as the amount of original sample for the water extraction needed would be at least four times as big {3}.

The other possible constituent of soluble salts that will hardly ever be analysed quantitatively, is the crystalline water. This has to be kept in mind, when comparing the results from the ion measurements with the weight loss of the sample after extraction.

4.2 Analytical methods used in this paper

Electrical conductivity and temperature were measured by means of a microprocessor conductometer Knick 702 without automatic temperature compensation, the measuring temperature never differed more than WC from 25°C. After these test series we however decided, to measure the electrical conductivity in future directly with temperature compensation for better comparability of the results.

The pH values were determined by means of a Knick-pH-Meter (type 646) with temperature compensation and an electrode Ingold type U 455.

For the filter photometry we used a photometer by Dr. Lange (type LP2W) with ready made cuvette tests for K^+ , Ca^{++} , Mg^{++} , NH_4^+ , Cl^- , NO_3^- , SO_4^{--} . Sodium was measured by means of a Na^+ selective electrode (Ingold pNa 205-1000/S7) attached to a WTW pH-ion-meter pMX3000/pH, which was calibrated before each series of measurements. The detection limits for these methods are given in table 1. In many cases the detection limits for potassium and for sulphate are too high. In addition to the high detection limit, the potassium measurement has a rather high analytical error of +/- 5 mg/l.

Table 1: Detection limits for the filter photometry tests and the sodium ion selective electrode measurements. (Values per unit sample, calculated for a sample to water ratio of 1:100)

	Na^+	K^+	Ca^{++}	Mg^{++}	NH_4^+	Cl^-	NO_3^-	SO_4^{--}
mg/l	1	8	0,1	0,5	0,02	1	1	40
$\mu\text{g/g}$ Sample	100	800	10	50	2	100	100	4000
$\mu\text{mol/g}$ Sample	4,3	20,5	0,2	2,1	0,1	2,8	1,6	41,6 ₁

For ion chromatography (analysed by Labor Jägers, Bomheim) a WATERS equipment was used (pump 510; injection block U6K, 481 UV-detector; at 254nm). The cations were separated on a Polyspher IC CA column, 100 [mm] long, 3,2 [mm] diameter (Fa. Merck) With pre-column, the solvent was 0,1 [mmol] Cer-III-sulphate-solution, fluctuation rate 1 [ml/min] and injected volume 20 [μl]. The anions were separated on a Polyspher IC AN-2 column, 120 [mm] long, 4,6 [mm] diameter (Fa. Merck) with pre-column, the solvent was 2 [mmol] sodiualizylate-solution, pH of 7,8 achieved by TRIS, fluctuation rate 1,3 [ml/min] and injected volume 50 [μl].

Flame photometry measurements and atomic absorption spectroscopy were performed at the university of Mainz, at the Institute of Geoscience.

5. PREPARATION OF SALT CONTAMINATED SAMPLES

To test our analytical method, we contaminated lime plaster samples with 0 to 20 [%] of salt as follows. It however has to be stated here, that we consider plaster samples of wall paintings that have salt contents of one or more percent as being highly contaminated by salts.

5.1 Lime plaster

The lime plaster was prepared out of slaked lime (1 part per unite volume) and a fine grained sand (3 parts per unite volume). This plaster was crushed and repeatedly humidified to enhance carbonation until its pH lay below 9 (phenolphthalein test {5}), to make sure that the remaining $\text{Ca}(\text{OH})_2$ content could be neglected. The wet chemical analysis of the plaster gave the following values [weight-%]: $\text{CO}_3 = 12,1$, $\text{Ca} = 8,5$, $\text{Mg} = 0,1$, HCl-insoluble residue = 77,1 (wet chemical analysis of lime mortar never sum up to 100% {4}).

5.2 Salt mixture 1

For the first salt mixture only salts were selected, that are not hygroscopic in normal laboratory environmental conditions (around 20 [°C] and 40-50 [%] relative humidity) and that, with the exception of gypsum, do not contain any crystalline water. Further salts were selected, that cannot form reaction products, that are less soluble than the initial salts, when brought into solution together. This first salt mixture did not contain any magnesium salt, as there exists no well soluble and water free magnesium salt. Salt mixture 1 [weight-%]:

23,45 %	NaNO_3	equals	25 %	NaNO_3
23,45 %	NaCl	equals	25%	NaCl
23,45 %	KNO_3	equals	25%	KNO_3
29,65 %	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	equals	25%	CaSO_4

5.3 Salt mixture 2

To the second salt mixture magnesium sulphate was added, to be able to also test the magnesium analysis. Epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) was used out of a jar that had been opened several month before. Epsomite has a very high equilibrium relative humidity (90,1 [%] at 20 [°C] {1}) and can loose its crystalline water in dry laboratory conditions to form hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) or Kieserit ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$). Thus the exact water content of the used magnesium sulphate is not known. As for the first mixture, the second should neither contain salts, that can form reaction products, that are less soluble than the initial salts, when brought into solution.

Salt mixture 2 [weight-%]:

15,84%	NaNO_3	equals	20%	NaNO_3
15,84%	NaCl	equals	20%	NaCl
15,84%	KNO_3	equals	20%	KNO_3
20,04%	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	equals	20%	CaSO_4
32,44%	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	equals	20%	Mg SO_4

5.4 Salt contaminated samples

Three different types of samples were prepared out of the lime plaster and the two different salt mixtures (list of samples see table 2 in the appendix):

SM1 = samples of the first salt mixture plus plaster

SM2 = samples of the second salt mixture plus plaster

oP1 = samples of salt mixture 1 without plaster

For the **SM1 and SM2** samples, plaster and salts were weighted air dry and thoroughly mixed for about 10 minutes by hand in an agate mortar, from this mixture the salts were then extracted as stated above.

The **oP** samples were prepared by just dissolving varying amounts of salt mixture 1 to demineralized water. This was done to cheque whether all salts would actually dissolve, even when present in high concentrations, and also to see whether the plaster had any influence on this.

For some samples with very high salt concentrations we prepared a second sample because the results of the chloride content of the first were somewhat intriguing.

6. RESULTS OF SAMPLES ARTIFICIALLY CONTAMINATED WITH SALT

All results of the water extraction analyses are listed in tables 3 to 5 in the appendix. Table 3 gives the raw data as it is measured in [mg/l extraction solution], in tables 4 and 5 these values are calculated into [μg] and [μmol] per gram of initial sample, respectively. Normally the result of the analysis are only given in these latter units. The [mg/l] values are needed to find out whether the measuring range of an analytical method to be selected fits the needs of salt contaminated samples from monuments, therefore they are given here.

The *pH of the water extraction* gives the concentration of OH^- and H_3O^+ and also on CO_3^{2-} or HCO_3^- respectively, as carbonate is dominating over HCO_3^- and CO_2 at pH-values above 10.3, hydrogen carbonate predominates at pH-values between 10.3 and 6.4 and CO_2 below 6.4 {6}. Hence, a high pH indicates, that OH^- and CO_3^{2-} are present in considerable amounts and low pH-values, that rather CO_2 and H_3O^+ are dominating.

All pH values from the water extraction of salt mixture 1 (table 3 samples SM1 and oP1) lie between 6 and 8, where as all the pH's of the samples containing magnesium (SM2) are between 9 and 10. To our experience the pH values of water extractions from lime plaster samples from monuments usually lie in the same range of order, between 6 and 10.

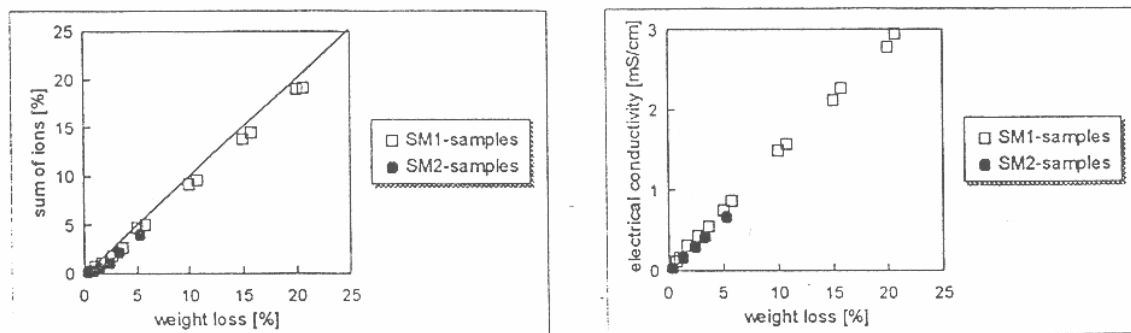
The *weight loss* of the sample after the water extraction (wl in table 3) gives the total amount of ions plus crystalline water that were extracted from the sample. Therefore it is always bigger than the sum of the analysed ions (in table 4 soi is given in [$\mu\text{g/gPr}$], this figure divided by 10000 equals soi in

The diagonal line in figure 1 (left side) gives all the points in the plot, where weight loss would equal the sum of ions, all measured points lie below this line indicating, that weight loss of all samples was greater than the sum of measured ions.

Measurement of the *electrical conductivity* (ec in table 3) give a first indication on the ionic strength of the solution. If the value of the water extraction of a lime mortar or a limestone sample lies below 100 [$\mu\text{S/cm}$], the sample can be considered as "salt free". As every ion has its own equivalent electrical conductance, the values of the electrical conductivity of two solutions will be different if their ionic composition varies, even if they have the same total ion concentration. Figure 1 (right side) shows that there exists a very good correlation between weight loss and electrical conductivity for both salt mixtures.

Comparisons between electrical conductivity, sum of ions and weight loss can give indications on the quality of the salt analyses, in as much, that if two samples come from the same contamination conditions of one building, those three values should show good correlations. If not, the samples either contain completely different salt mixtures, or a major measuring error has occurred.

Figure 1: Comparisons between weight loss and sum of measured ions and electrical conductivity



respectively. (SM1-samples = samples SM1, oP1 and - only on the right plot - SM1W)

Plots of all analysed and calculated (theor. value SM1 respectively SM2) ion concentrations of the extracted solutions are given in figure 2 (for the exact values see table 3). It can be seen that all measurements show the right trend, however there are slight differences in accuracy for each ion.

The measured *sodium* values were usually somewhat lower than the calculated value with the difference being bigger for lower values.

As mentioned above the *potassium* measurement we used has quite a high analytical error, which is clearly visible in figure 2, the measurements nevertheless seem to show a good trend, although in the samples containing 20% of salt, the measured value of potassium is 10% higher than the value theoretically calculated (compare samples "SM1/20" to "soll SM1/20" in table 3).

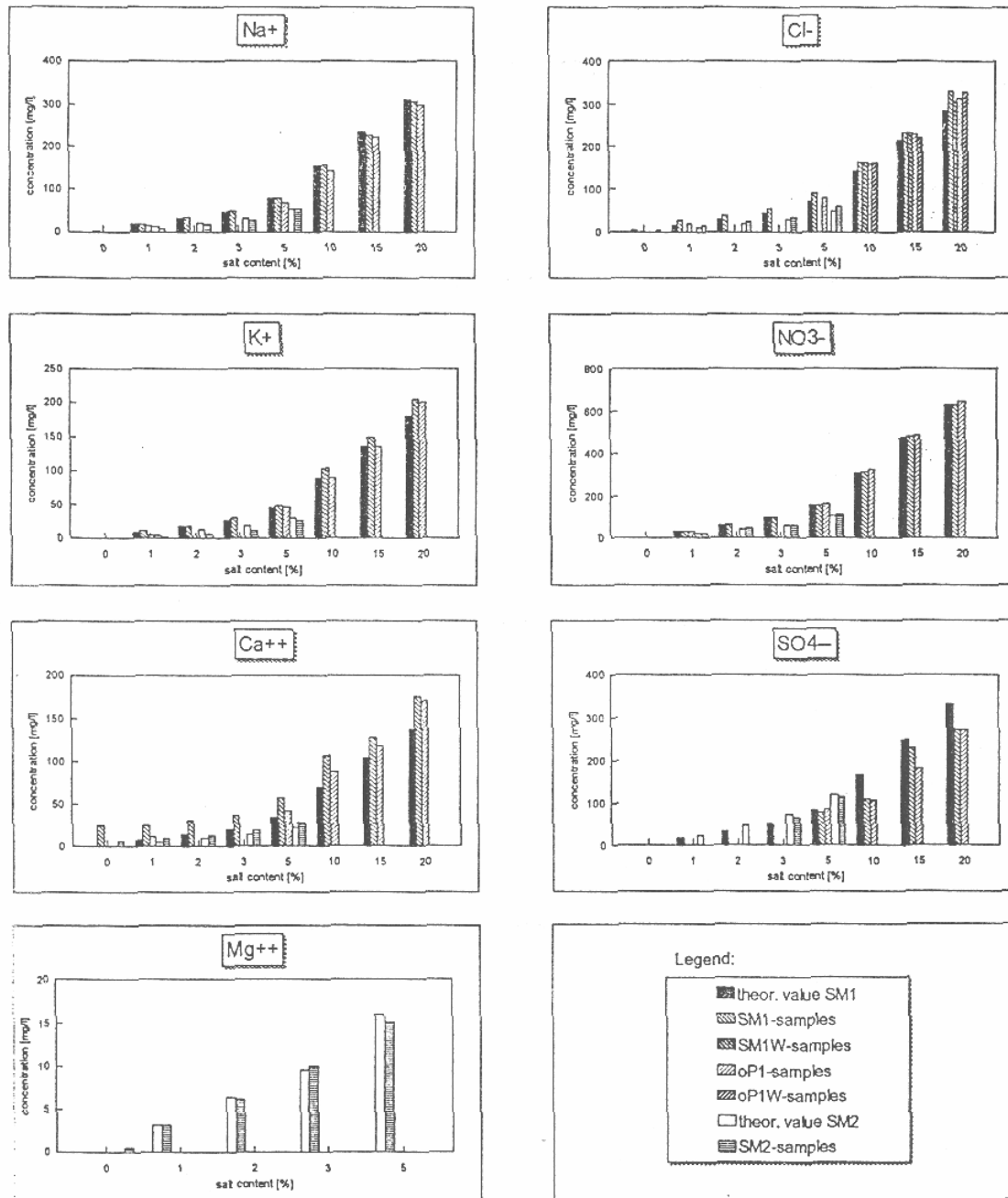


Figure 2: Contents of each ion in the solution in [mg/l] plotted as bars, grouped for samples of the same total salt content (see also table 3).

Water extractions from lime plasters or limestone always do contain some calcium. The two salt free samples that were analysed here (SM1/0; SM2/0) give very different water extractable calcium contents, although they are two fragments from exactly the same plaster sample, and the water extraction was done following the same procedure. The calcium analysis performed with the photometry tests gave all much-higher readings than the theoretical values, even for the samples that did not contain plaster (oP1-samples). Again these measurements give the right trend,

Magnesium was only measured for the samples containing a magnesium salt and for one salt free sample (SM2/0). From the salt free sample, it can be seen, that the plaster itself contains a little bit of water extractable magnesium. The used analysing method gives quite accurate values within the tested ranges of salt contamination.

In a first series of measurements all *chloride* values of the samples with high salt content were considerably higher than the theoretical values, therefore a second series of samples (SM1W) was prepared to only measure chloride. Again the measured values were higher than the theoretical ones.

The *nitrate* measurements revealed to be the most accurate ones out of the ions tested, with usually giving values only a little above the calculated ones.

The detection limit for sulphate of the photometry tests we used showed to be too high for all samples containing less than 3 [%] of salt. For the samples with a higher total salt concentration the sulphate test always gave too low values.

Although there was no *ammonia* containing salt added to the samples, all ammonia measurements gave values between 3 and 7 [$\mu\text{g/g}$] of sample, which indicates, that ammonia contents of that order can be considered not contaminated.

For all the ions it can be stated, that the analysed values reflect the right order of magnitude of the concentration, but that the error for individual ions can be considerable. This is also reflected in the value of the *ionic balance* (ib in table 5). It is calculated by subtracting the sum of measured negative charges from the sum of measured positive charges (values in [$\mu\text{mol/g}$] of sample), for the ions analysed in this paper following the equation:

$$\text{ib} = [\text{Na}^+] + [\text{K}^+] + (2 * [\text{Ca}^{++}]) + (2 * [\text{Mg}^{++}]) + [\text{NH}_4^+] - [\text{Cl}^-] - [\text{NO}_3^-] - (2 * [\text{SO}_4^{--}])$$

If all ions present are analysed the ionic balance should be zero. As stated above e.g. hydrogen carbonate is usually present in the water extract (partly dissolution of calcite) but not analysed, hence the ionic balance more often shows positive than negative values. In our experiments negative ionic balances are only achieved in samples with very high total salt concentration (see table 5), where actually the contents of all the anions could be established and hence the analytical errors summed up accordingly. In our analysis we consider a ionic balance to be satisfactory if it does not exceed 10% of the sum of all measured charges, if all ions are present in higher concentration than their detection limit. Compare e.g. "SM1/2" and "soll SM1/2" in table 5, where the ionic balance would be 70 [$\mu\text{mol/g}$] lower for SM1/2 if sulphate would have been detected accurately.

7. COMPARISON BETWEEN DIFFERENT MEASURING METHODS

To compare the results of our measuring equipment with other analytical methods seven water extraction samples from highly salt contaminated plaster at the church of St. Maria im Kapitol, Köln were analysed using flame photometry (**FPM**) for sodium, potassium and calcium and atomic absorption spectroscopy (**AAS**) for magnesium and ion chromatography (**IC**) for all the ions (table 6). As the analysis could not be done all at the same day the samples were kept in the refrigerator in between the different analysis and only brought to room temperature shortly before measurement.

The results are given graphically in figure 3. It can be seen there, that for *chloride*, *nitrate* and *calcium* the results of all methods are quite close. The readings for chloride are usually higher for the Lange filter photometry (**LFP**) than the **IC**, which is in good coincidence with the fact, that chloride measurements in the artificial samples were always higher than the theoretically calculated values.

Again the detection limit for sulphate when using filter photometry revealed to be too high (please note, that out of the seven samples only four were analysed using **LFP** due to lack of enough solution! - see table 6).

The *magnesium* analysis by **AAS** and **IC** give approximately the same values, the **LFP** however gives values that are usually much lower. This is in contradiction to the magnesium measurements achieved on the artificial samples (SM2 in figure 2), where the magnesium measurements matched nearly exactly the theoretical values. For very high sodium contents the analysis given by **IC** are twice as big as the concentrations measured by **ISE** or **FPM**, for low sodium contents all three methods give very similar results. By using **LFP** in none of the seven samples potassium could be detected, because of the rather high detection limit. **IC** gives much larger potassium values than **FPM** in the highly salt contaminated samples and similar values in samples containing somewhat less salt.

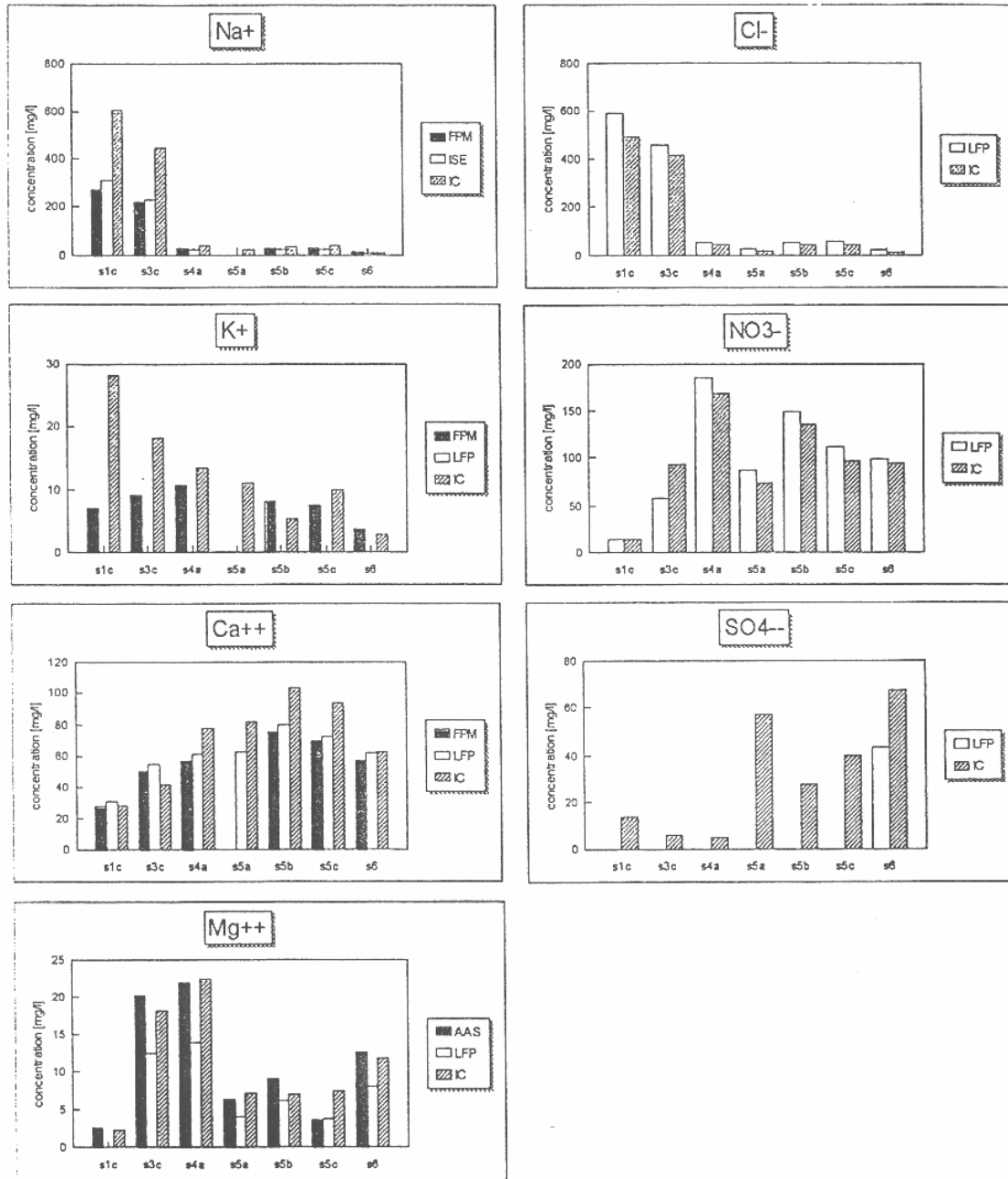


Figure 3: Comparison between different methods for analysing the same extracted solutions (**FMP** = flame photo meter; **AAS** = Atomic absorption spectroscopy; **ISE** = sodium ion selective electrode; **LFP** = Lange filter photometer; **IC** = ion chromatography; values in table 6)

8. CONCLUSIONS

The analysis have shown, that the results achieved by the water extraction method of plaster samples, seem to be dependent on the method used for analysing the solution. For total salt contents below 5% all methods seem to give the right order of magnitude of salt content. For more highly contaminated samples the water extract should probably be diluted prior to analysis.

Measurements of the electrical conductivity of the solution and of the weight loss of the samples after the water extraction give very good indications on the total amount of salts present.

The filter photometry tests as well as the sodium ion selective electrode performed generally very well in our tests, and seem to be a good alternative to more expensive equipment. It has however to be said that the ion selective electrode needs constant care and calibration before each series of measurements.

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REFERENCES

- {1} Arnold, A., Zehnder, K. (1991): Monitoring wall paintings affected by soluble salts. - The Conserv. of Wall Paintings, Sympos. by Courtauld Inst. of Art a.the Getty Conserv. Inst., London, July 13-16, 1987, p. 103-135.
- {2} Blanco Varela, M. T., Menendez, E., Hoyos, M. (1991): Study of surface decay of the marbles and serpentine from the Descalzas Reales convent at Madrid. - La conservation des monuments dans le bassin méditerranéen, Actes du 2ème symp. int, 19.-21. Nov., Genève, 167-175.
- {3} Bläuer, C. (1987): Verwitterung der Berner Sandsteine. - PhD-Thesis Univ. Bern.
- {4} Bläuer Böhm, C., Jägers, E. (1996): Analysis and recognition of dolomitic lime mortars. in press. Int. Kolloquium on Roman Wall Paintings, Fribourg 7.-9. März 1996.
- {5} Henning, O., Knöfel, D. (1989): Baustoffchemie: eine Einführung für Bauingenieure und Architekten. 4. durchgesehene Aufl. - VEB Verl. f. Bauwesen, Berlin.
- {6} Hütter, L. (1994): Wasser und Wasseruntersuchung. - Salle, Frankfurt a.M., 515 S.
- {7} IFS (1993): IFS-Projekt "Naturstein kataster" - Untersuchungsvorschriften Stand 9.2.93. - Unpubl. script.
- {8} Matteini, M. (1991): In review: an assessment of florentine methods of wall painting conservation based on the use of mineral treatments. - The Conserv. of Wall Paintings, Sympos. by the.Courtauld Inst. of Art and the Getty Conserv. Inst., London, July 13-16, 1987, p. 137-148.
- {9} Monte, M. Del, Sabbioni, C. (1983): Weddellite on limestone in the Venice environment. - Environ. Sci. Technol., Vol. 17, pp. 518-522.
- {10} RILEM 25-PEM (1980): Essais recommandés pour mesurer l'altération des pierres et évaluer l'efficacité des méthodes de traitement. - Matériaux et Constructions 13, N. 75, 175-253.
- {11} Rösch, H., Schwarz, H.-J. (1994): Salzsäuren in der Kreuzkirche Pilsun. - Hrsg. C. Segers-Glocke, BMFT-Forschungsprojekt Wandmalerei-Schäden, Schlussber. interdisziplinäre Ergebnisse. CW Niemeyer Verlag, Hameln, 115-118.
- {12} Umierski, H., Brüggerhoff, St., Mirwald, P.W. (1989): Untersuchungen zur Probenahme und Analyse von Porenwässern aus Natursteinen. - Jahresber. a. d. Forschungsprogr. Stefznerfall-Steinkonservier., Bd. 1, 1989, S. 131-145.
- {13} Zehnder, K. (1982): Verwitterung von Molassesandsteinen an Baudenkmalern und Naturaufschlüssen. -Beitr. Geol. Schweiz., geotech. Ser., 61.

Appendix

Table 2: List of samples artificially contaminated with salts, with indication of what was measured on each sample (SM1 = samples of the first salt mixture and plaster; SM2 = samples of the second salt mixture and plaster; oP = saltmixture 1 dissolved in water without mixing it first with plaster; W = repetition of water extract)

sample	plaster [g]	amount of salt [g]	salt content [%]	anions	cations except Mg ⁺⁺	Mg ⁺⁺	chloride
SM1/0	1,00	0	0	+	+		
SM1/1	0,99	0,01	1	+	+		
SM1/2	0,98	0,02	2	+	+		
SM1/3	0,97	0,03	3	+	+		
SM115	0,95	0,05	5	+	+		
SM1/10	0,90	0,10	10	+	+		
SM1/15	0,85	0,15	15	+	+		
SM1/20	0,80	0,20	20	+	+		
SM1/10W	0,90	0,10	10				+
SM1/15W	0,85	0,15	15				+
SM1/20W	0,80	0,20	20				+
oP1/1	0	0,01	-	+	+		
oP1/5	0	0,05	-	+	+		
oP1/10	0	0,10	-	+	+		
oP1/15	0	0,15	-	+	+		
oP1/20	0	0,20	-	+	+		
oP1/10W	0	0,10	-				+
oP1/15W	0	0,15	-				+
oP1/20W	0	0,20	-				+
SM2/0	1,00	0	0	+	+	+	
SM2/1	0,99	0,01	1	+	+	+	
SM2/2	0,98	0,02	2	+	+	+	
SM2/3	0,97	0,03	3	+	+	+	
SM2/5	0,95	0,05	5	+	+	+	

Table 3: Analysis of samples artificially contaminated with salts in [mg/l-solution] when 1 g of sample is extracted with 100ml of water. (ec = electrical conductivity, wl = weight loss, Soll-samples = theoretically calculated values)

sample	pH	ec	wl	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	NH ₄ ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻
	-	[μS/cm]	[%]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]
SM1/1	6,8	319	1,69	16	11	25		0,050	26	32	<40
SM1/2	6,8	429	2,67	34	18	30		0,036	38	65	<40
SM1/3	6,9	548	3,64	48	29	36		0,036	54	97	<40
SM1/5	6,2	865	5,76	81	48	57		0,030	90	153	79
SM1/10	6,0	1573	10,73	156	104	107		0,037	164	317	110
SM1/15	5,9	2270	15,69	227	149	128		0,058	234	478	229
SM1/20	5,9	2950	20,67	308	205	176		0,066	331	629	272
SM1/0	6,1	118	0,76	1	<8	25		0,037	3	<1	<40
SM1/10W	8,2	1485	10,31						164		
SM1/15W	7,8	2150	15,29						233		
SM1/20W	7,5	2770	20,25						308		
oP1/1	7,0	170		13	<8	12		0,038	19	32	<40
oP1/5	6,5	757		68	46	41		0,048	81	158	84
oP1/10	6,4	1478		142	91	87		0,052	158	328	108
oP1/15	6,6	2120		222	136	118		0,044	231	483	181
oP1/20	6,6	2780		298	200	171		0,038	313	649	272
oP1/10W	6,5	1451							161		
oP1/15W	6,5	2120							221		
oP1/20W	6,5	2770							328		
soll SM1/1			1,00	16	9	7		0	14	32	17
soll SM1/2			2,00	31	18	14		0	29	63	33
soll SM1/3			3,00	47	27	21		0	43	95	50
soll SM1/5			5,00	78	45	35		0	71	154	83
soll SM1/10			10,00	156	91	69		0	142	315	166
soll SM1/15			15,00	236	136	104		0	213	472	248
soll SM1/20			20,00	311	181	138		0	285	630	331
SM2/0	9,8	41	0,37	<1	<8	6	0,5		3	<1	<40
SM2/1	9,7	173	1,40	7	<8	10	3,2		14	22	<40
SM2/2	9,3	302	2,40	18	<8	13	6,2		25	48	<40
SM2/3	9,1	420	3,33	26	11	19	10,1		35	61	64
SM2/5	9,0	669	5,30	52	27	28	15,1		57	108	115
Soll-SM2/1			1,00	11	6	5	3,2	0	10	21	24
Soll-SM2/2			2,00	21	12	9	6,4	0	19	43	48
Soll-SM2/3			3,00	32	18	14	9,6	0	29	64	72
Soll-SM2/5			5,00	53	31	23	16	0	48	106	119

Table 4: Analysis of samples artificially contaminated with salts in [$\mu\text{g/g}$ of sample] = [$\mu\text{g/gPr}$]
(soi = sum of ions)

sample	Na ⁺ [$\mu\text{g/gPr}$]	K ⁺ [$\mu\text{g/gPr}$]	Ca ⁺⁺ [$\mu\text{g/gPr}$]	Mg ⁺⁺ [$\mu\text{g/gPr}$]	NH ₄ ⁺ [$\mu\text{g/gPr}$]	Cl ⁻ [$\mu\text{g/gPr}$]	NO ₃ ⁻ [$\mu\text{g/gPr}$]	SO ₄ ⁻⁻ [$\mu\text{g/gPr}$]	soi [$\mu\text{g/gPr}$]
SM1/1	1550	1130	2540		5,0	2640	3160	<4000	11025
SM1/2	3360	1810	3030		3,6	3820	6490	<4000	18514
SM1/3	4770	2940	3620		3,6	5370	9730	<4000	26434
SM1/5	8070	4830	5700		3,0	8990	15300	7870	50763
SM1/10	15600	10400	10700		3,7	16400	31700	11000	95804
SM1/15	22700	14900	12800		5,8	23400	47800	22900	144506
SM1/20	30800	20500	17600		6,6	33100	62900	27200	192107
SM1/0	142	<800	2500		3,7	344	0	<4000	2990
SM1/10W						16400			
SM1/15W						23300			
SM1/20W						30800			
oP1/1	1270	<800	1200		3,8	1890	3230	<4000	7594
oP1/5	6750	4620	4110		4,8	8120	15800	8420	47825
oP1/10	14200	9070	8740		5,2	15800	32800	10800	91415
oP1/15	22200	13600	11800		4,4	23100	48300	18100	137104
oP1/20	29800	20000	17100		3,8	31300	64900	27200	190304
oP1/10W						16100			
oP1/15W						22100			
oP1/20W						32800			
soil SM1/1	1570	910	690		0	1420	3150	1650	9390
soil SM1/2	3110	1810	1380		0	2850	6290	3310	18750
soil SM1/3	4670	2720	2070		0	4270	9450	4960	28140
soil SM1/5	7780	4530	3450		0	7110	15440	8270	46580
soil SM1/10	15570	9070	6900		0	14230	31490	16550	93810
soil SM1/15	23550	13600	10350		0	21340	47230	24820	140890
soil SM1/20	31130	18140	13810		0	28450	62970	33090	187590
SM2/0	<100	<800	590	50		330	<100	<4000	970
SM2/1	670	<800	990	320		1400	2210	<4000	5590
SM2/2	1780	<800	1340	620		2490	4760	<4000	10990
SM2/3	2560	1105	1900	1010		3460	6122	6440	22597
SM2/5	5220	2731	2770	1510		5720	10836	11500	40287
Soil-SM2/1	1050	610	470	320	0	960	2130	2400	7940
Soil-SM2/2	2100	1230	930	640	0	1920	4250	4760	15830
Soil-SM2/3	0	1840	1400	960	0	2890	6380	7150	23780
Soil-SM2/5	5260	3060	2330	1600	0	4810	10640	11910	39610

Table 5: Analysis of samples artificially contaminated with salts in [$\mu\text{mol/g}$] of sample = [$\mu\text{mol/g}$] (ib = ionic balance)

sample	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	NH ₄ ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻⁻	ib
	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]	[$\mu\text{mol/g}$]
SM1/1	67	29	63		0,3	75	51	<42	98
SM1/2	146	46	76		0,2	108	105	<42	131
SM1/3	208	75	90		0,2	152	157	<42	155
SM1/5	351	124	142		0,2	254	247	82	95
SM1/10	679	266	267		0,2	463	511	115	276
SM1/15	987	381	319		0,3	660	771	238	100
SM1/20	1340	524	439		0,4	934	1014	283	228
SM1/0	6	<20	62		0,2	10	0	<42	121
SM1/10W						463			
SM1/15W						657			
SM1/20W						869			
oP1/1	55	<20	30		0,2	53	52	<42	11
oP1/5	294	118	103		0,3	229	255	88	-42
oP1/10	618	232	218		0,3	446	529	112	87
oP1/15	966	348	294		0,2	652	779	188	95
oP1/20	1296	512	427		0,2	883	1047	283	166
oP1/10W						454			
oP1/15W						623			
oP1/20W						925			
soll SM1/1	68	23	17		0	40	51	17	1
soll SM1/2	135	46	34		0	80	101	35	0
soll SM1/3	203	70	52		0	120	152	52	0
soll SM1/5	338	116	86		0	201	249	86	5
soll SM1/10	677	232	172		0	401	508	172	0
soll SM1/15	1024	348	258		0	602	762	258	8
soll SM1/20	1354	464	345		0	803	1016	345	0
SM2/0	<4	<20	15	2		9	<1,6	<42	24
SM2/1	29	<20	25	13		39	36	<42	30
SM2/2	77	<20	33	26		70	77	<42	48
SM2/3	ill	28	47	42		98	99	67	-13
SM2/5	227	70	69	62		161	175	120	-16
Soll-SM2/1	46	16	12	13	0	27	34	25	0
Soll-SM2/2	91	31	23	26	0	54	69	50	0
Soll-SM2/3	137	47	35	39	0	82	103	74	0
Soll-SM2/5	229	78	58	66	0	136	172	124	0

Table 6: Comparison between the values measured using different methods for analysing the same water extractions (FPM/AAS = flame photo meter for Na, K and Ca, and Atomic absorption spectroscopy for Mg; ISE/LFP = sodium ion selective electrode and Lange filter photometer; IC = ion chromatography; soi = sum of measured ions; ib = ionic balance; not all methods could be applied to all solutions because some samples were too small)

Sample	Methode	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ⁻	soi	ib
		[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[µg/gPr]	[µmol/gPr]
s1c	FPM/AAS	271	7	28	3					
s3c	FPM/AAS	218	9	50	20					
s4a	FPM/AAS	26	11	57	22					
s5a	FPM/AAS				6					
s5b	FPM/AAS	25	8	76	9					
s5c	FPM/AAS	27	8	70	4					
s6	FPM/AAS	10	4	57	13					
s1c	ISE/LFP	310	0	31	0	593	15		95185	-177
s3c	ISE/LFP	227	0	55	13	459	59		81 176	-25
s4a	ISE/LFP	22	0	62	14	53	185	0	33525	72
s5a	ISE/LFP		0	63	4	26	87		18050	140
s5b	ISE/LFP	21	0	80	6	53	149	0	30883	149
s5c	ISE/LFP	23	0	73	4	58	111	0	26763	151
s6	ISE/LFP	7	0	62	8	20	100	43	30140	127
s1c	IC	604	28	28	2	493	15	14	118464	1415
s3c	IC	446	18	42	18	413	93	6	103549	1014
s4a	IC	34	13	77	23	40	169	5	36013	357
s5a	IC	20	11	82	7	18	74	57	26887	292
s5b	IC	30	5	103	7	40	135	28	34770	329
s5c	IC	38	10	94	8			40	32913	359
s6	IC	6	3	63	12	151	94	68	32475	137