

## **Common salt mixtures database: a tool to identify research needs**

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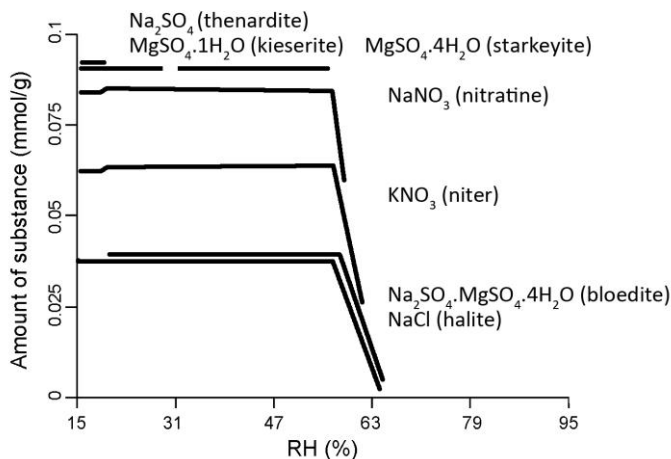
### **Abstract**

Salt mixtures found in building materials and stone sculptures have been analyzed in the Monuments Laboratory at KIK-IRPA since the early 1960's. The common salt mixtures database is a spreadsheet based on the results of quantitative ion analyses carried out with Ion Chromatography at KIK-IRPA since 2004, currently counting almost 6000 records of samples from Belgian monuments and sculptures, e.g., about 1600 brick and mortar samples, 300 wall plaster and 581 natural stone samples. Today, approximately 500 samples are yearly analyzed and added to the database. The samples are classified by location, type of material, depth and height. The main objective of this database is to generate average compositions of salt mixtures according to different criteria such as the geographic region, the type of building material, the depth and the height and hence to narrow down specific research needs and move from single salts to relevant salt mixtures. The average ion content representative for a selected group of samples is entered into the program ECOS/RUNSALT to predict the crystallization behavior. The outputs reveal a complex mixture consisting of kieserite, starkeyite, thenardite, nitratine, niter, darapskite, halite, bloedite and aphanthalite. Ultimately the location data will be linked to a geographic information system (GIS) and the database will be made available online so that researchers active in the field of salt analyses can add data.

**Keywords:** salt, database, conservation, monuments, ecos

## 1 Introduction

A database was established containing quantitative ion data of the aqueous extract of powder samples lifted from Belgian monuments since 2004. The database currently contains the results of almost 6000 samples classified among others by date, location, material type, depth and height. From the database common occurring salt mixtures can be derived according to selected criteria. For example, from a total of 244 brick samples lifted from the first centimeter at a height up to 30 cm from the floor level, an average ion composition can be calculated. This data can then be entered into the RUNSALT software [1] based on the thermodynamic model ECOS (Environmental Control of Salts) [2]. The output represents in this specific case the salt crystallization behavior of the average ion mixture typical for the first cm of brick at a height up to 30 cm, consisting of halite, bloedite, niter, nitratine, starkeyite, kieserite and thenardite (Figure 1) with a total average content of 0.64 wt%. This result is obtained after a correction for an excess of calcium ions, which corresponds to approximately 0.08 wt% and also excluding gypsum to an average extent of approximately 1.26 wt%. The main objective of the database is to generate the average composition of salt mixtures according to different criteria such as the geographic region, the type of building material, the depth and the height and thus to narrow down specific research needs and move from single salts to relevant salt mixtures.



**Figure 1:** ECOS/RUNSALT output (25°C) derived from the average ion composition of 244 brick samples lifted in the 1<sup>st</sup> cm at a height up to 30 cm in Belgian monuments. A correction for an excess of calcium ions is applied and gypsum was removed

## 2 Sampling procedure

Most of the samples have been lifted from building materials by powder drilling (diameter: 5 mm) into the substrate at different depths and heights. The powdered samples are individually and hermetically sealed in pre-weighed containers and transported to the laboratory. The ambient moisture content is determined gravimetrically by weighing the samples at 60°C until a constant weight is reached. Then the samples are conditioned at 20°C and 95% RH to determine the hygroscopic moisture content. The weight increase is related to that of the dry sample and presented as weight percentage (wt%).

The salt content is determined by adding approximately 1 g of the dried sample to 100 ml pure water, which is mixed to extract soluble ions. The quantity of anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) and cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) of the filtered extract is analyzed with Ion Chromatography (IC, Metrohm). The results in parts per million (ppm) are converted into milli-equivalents/g and presented as wt%. The data expressed as millimole per gram (mmol/g) are entered into the ECOS/RUNSALT thermodynamic model. Currently this is done for the average ion content of a selected group of samples.

## 3 Database setup

The spreadsheet database is arranged into two pages. The first page contains the entire dataset while the second page the legend with abbreviations used.

The sample data include a Sample Code, the analytical methods used, such as, Ion Chromatography (IC), X-Ray Diffraction (XRD), Raman Spectroscopy and/or the ambient- and hygroscopic moisture content, the month and year when the sample was lifted, the location by “city”, the “object” describing the type of artefact (monument, archaeological site, sculpture, ...), and, if applicable, information related to the documentation method of the institution having performed the investigation.

The following columns contain the material type, sampling height and depth. These data are completed with a code as described in Table 1. The numerical data related to the weight of the sample container, the initial sample weight, its weight after drying as well as after conditioning at 20°C and 95% RH, the weight of the dried sample used for analysis with IC, the amount of pure water added to bring the ions into solution and the data derived from the analysis with IC in ppm are included as well.

The ion concentrations are converted into milli-equivalents per gram (mEq/g), useful to interpret possible connections between anions and cations and to evaluate the balance between the two. An excess of  $\text{Ca}^{2+}$  ions is generally identified due to a small amount of  $\text{CaCO}_3$  dissolved from the substrate or to the presence of non-carbonated lime. A further

imbalance can be associated with the presence of sodium carbonate, which is further confirmed by a slight increased pH around 8, if so; the amount of  $\text{NaCO}_3$  in wt% is calculated. Further, the amount of gypsum is calculated. The database includes the input data (mmol/g) for the ECOS/RUNSALT model followed by the results of XRD and Raman Spectroscopy analyses of efflorescence lifted in-situ, if available.

The legend is found on the second page of the database. It contains for example the parameters related to the sampling: materials, depth, height and their codes (Table 1).

**Table 1:** sampling parameters and their codes used in the database

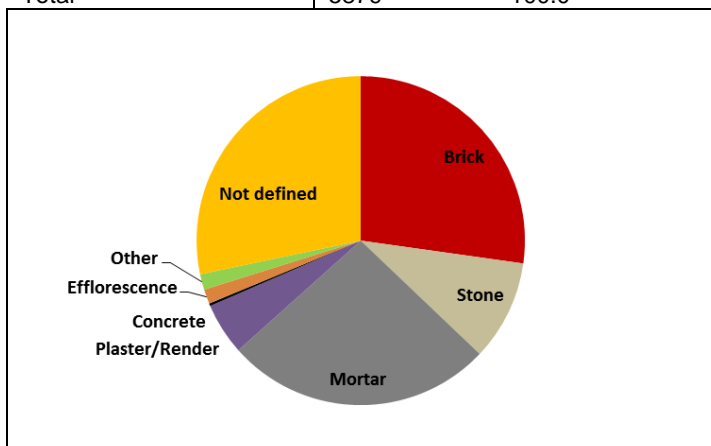
Materials	Code	Depth (cm)	Code	Height (cm)	Code
Efflorescence	E	Efflorescence	0	Low 0 to 30	L
Plaster (indoors)	P	0 to 1	1	Middle low 30 to 60	Mi
Render (outdoors)	R	0 to 2	2	Middle high 60 to 100	MiHi
Wall painting	W	0 to 3	3	High >100 <600	Hi
Brick	B	1 to 3	4	Vault or wall >600	T
Mortar/Joint	M	2 to 5	5		
Stone	S	3 to 5	6		
Earth/Soil/Dirt	D	5 to 7	7		
Concrete	C	7 to 10	8		

#### 4 Database content and calculations

The database currently contains the results of 5879 samples that can be split up among different types of materials (Table 2). The largest group, entitled “not defined”, relates to samples for which their identification is missing. The brick samples constitute the second largest group, followed by mortar, stone and plaster/render. Less than 5% can be associated with other materials, efflorescence and concrete.

**Table 2:** Distribution of the samples

Substrate	Amount	Percentage
Brick	1600	27.2
Stone	581	9.9
Mortar	1546	26.3
Plaster/Render	300	5.1
Concrete	15	0.3
Efflorescence	84	1.4
Other	90	1.5
Not defined	1663	28.3
Total	5879	100.0



To establish a statistical evaluation of the data, both the numerical and alphanumeric data were transferred and classified from the database to Matlab. In Matlab a graphical user interface was developed to represent a user-defined selection of the data, i) the frequency distribution of the samples for a selected parameter (amount of salt, anions, cations or individual ions) and ii) the correlation between two ions of choice, presented in a 2D-graph. The criteria for data grouping are the type of substrate and the sampling height and depth.

## 5 Statistical analysis of the salt data

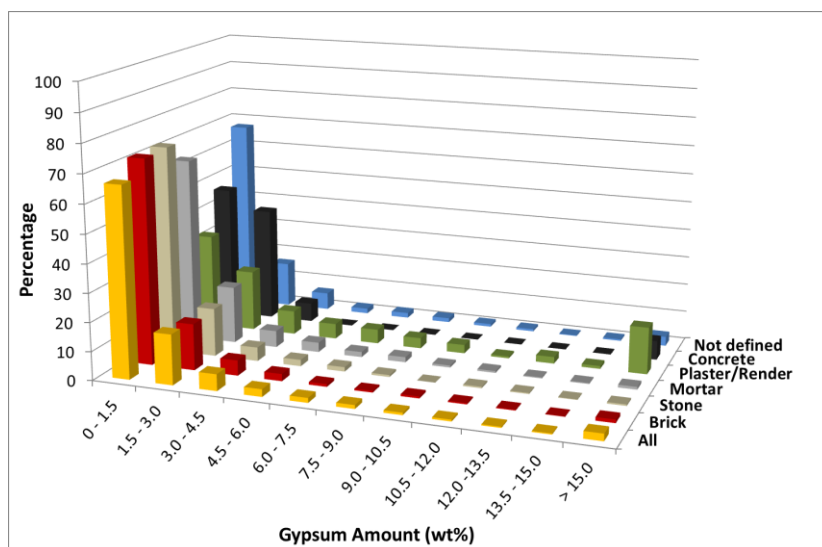
### 5.1 Average salt concentrations

The average ion concentration of anions and cations, expressed in milli-equivalents per gram (mEq/g), for each type of material is given in Table 3. For all material types, the average total amount of cations is in excess of the anion amount.

The average total ion content is noticeably higher for the group of plasters and renders, and decreases significantly for the mortars followed by both bricks and stones. This difference can be associated with a higher gypsum content, which is regularly detected in plasters and renders (Figure 2). Only 33% of these samples contain less than 1,5 wt% of gypsum, against 64,2% for the mortar samples. Nevertheless, the amount of samples containing at least 1,5 wt% of gypsum in stone and brick is considerably high, respectively 27,7% and 28,3%.

**Table 3:** Average concentration of anions and cations (mEq/g)

	<b>Brick</b>	<b>Stone</b>	<b>Mortar</b>	<b>Plaster/Render</b>	<b>All</b>
Anions	0.273	0.248	0.386	1.344	0.522
Cations	0.312	0.300	0.441	1.517	0.607
Total	0.584	0.548	0.827	2.861	1.129

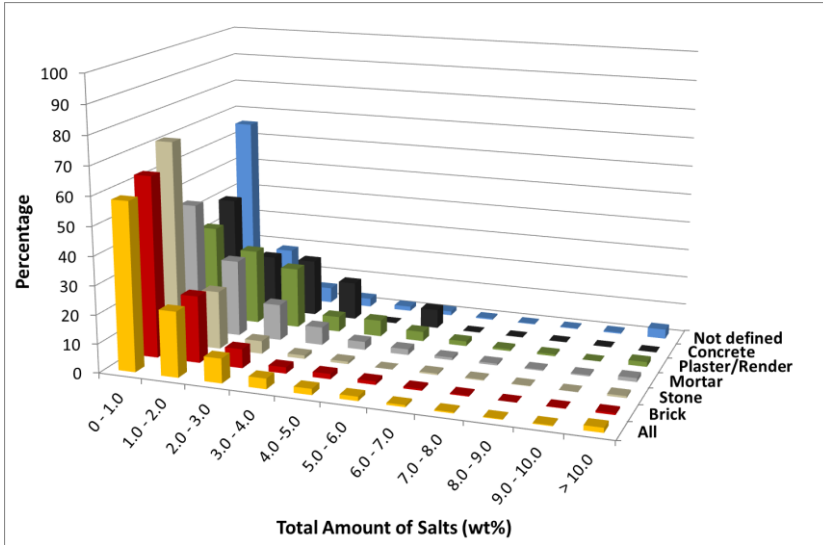


**Figure 2:** The frequency distribution of the gypsum content within different material types

The brick and stone samples contain similar average total salt concentrations, approximately 3.91 wt%, while the average increases for mortar samples to 2,86 wt% and up to 9,68 wt% for the plaster and render sample group (Table 4). When comparing the total amounts of salts, excluding gypsum (Figure 3), the same trend can be noticed. However, for the renders and plasters the amount of salts now only doubles instead of quadruples, explained by their high gypsum load.

**Table 4:** Average salt concentrations in wt%

	Brick	Stone	Mortar	Plaster/Render	All
Total	2.00	1.88	2.86	9.68	3.91
Total (excl. gypsum) (approximation)	0.83	0.87	1.38	1.82	1.77



**Figure 3:** The frequency distribution of the total amount of salts, excluding gypsum, for the different material types

### 5.2 Treatment of the average ion concentrations

It becomes even more interesting when looking at the crystallization behavior of the average ion mixtures, shown in Table 5, as examined with ECOS/RUNSALT. Three approaches can be distinguished. The first approach (Figure 4) is derived from the average ion mixture of all the samples. All salts presented in Table 6 show up in the output, with the exception of starkeyite.

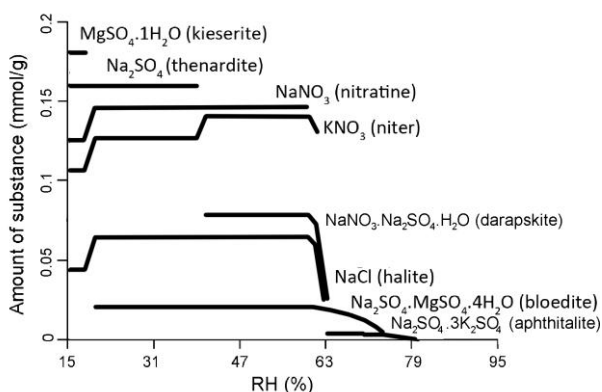
**Table 5:** Average ion concentrations (mmol/g)

Ion	Overall	Brick	Stone	Mortar	Plaster/Render
Chlorides	0.0441	0.0391	0.0146	0.0634	0.0481
Nitrate	0.0822	0.0430	0.0253	0.0750	0.0880
Sulphate	0.1978	0.0952	0.1042	0.1236	0.6038
Sodium	0.1329	0.0642	0.0790	0.1030	0.1866
Potassium	0.0626	0.0233	0.0266	0.0429	0.0468
Calcium	0.1424	0.0867	0.0656	0.1103	0.5400
Magnesium	0.0209	0.0058	0.0058	0.0095	0.0152



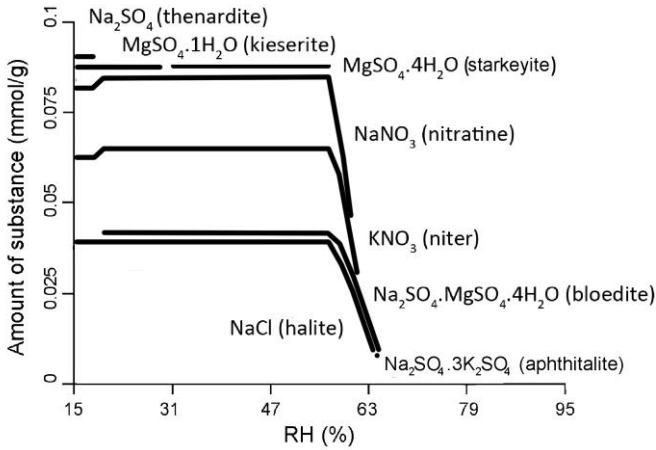
**Table 6:** Salts present in the ECOS/RUNSALT outputs based on the average ion contents (table 5). (✓: present in the output; —: not present in the output)

Salts	All	Brick	Stone	Mortar	Plaster/ Render
MgSO <sub>4</sub> .1H <sub>2</sub> O (kieserite)	✓	✓	✓	✓	✓
MgSO <sub>4</sub> .4H <sub>2</sub> O (starkeyite)	—	✓	—	✓	—
Na <sub>2</sub> SO <sub>4</sub> (thenardite)	✓	✓	✓	✓	✓
NaNO <sub>3</sub> (nitratine)	✓	✓	—	✓	✓
KNO <sub>3</sub> (niter)	✓	✓	✓	✓	✓
NaNO <sub>3</sub> .Na <sub>2</sub> SO <sub>4</sub> .H <sub>2</sub> O (darapskite)	✓	—	✓	—	✓
NaCl (halite)	✓	✓	✓	✓	✓
Na <sub>2</sub> SO <sub>4</sub> .MgSO <sub>4</sub> .4H <sub>2</sub> O (bloedite)	✓	✓	✓	✓	✓
Na <sub>2</sub> SO <sub>4</sub> .3K <sub>2</sub> SO <sub>4</sub> (aphthitalite)	✓	✓	✓	✓	✓



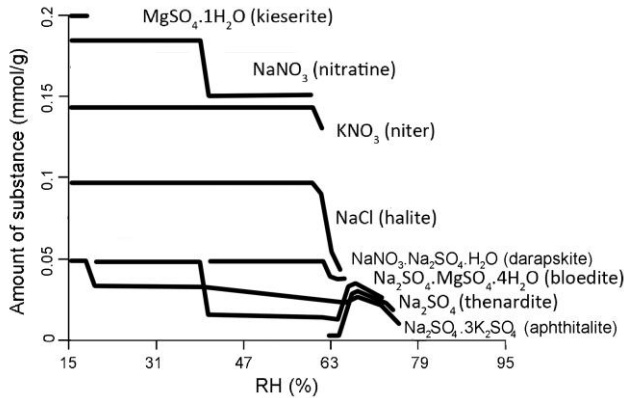
**Figure 4:** ECOS/RUNSALT output (25°C) of the average ion composition of all 5879 samples (table 5). Gypsum was removed from the ion mixture.

A second approach is based on the average ion concentration representative for the group of the brick samples (Figure 5). The output contains all the salts presented in Table 6, with the exception of darapskite in this case. A similar output is derived for the average ion mixture typical for the mortar samples.



**Figure 5:** ECOS/RUNSALT output (25°C) of the average ion composition of the brick samples (table 5), after correction for gypsum.

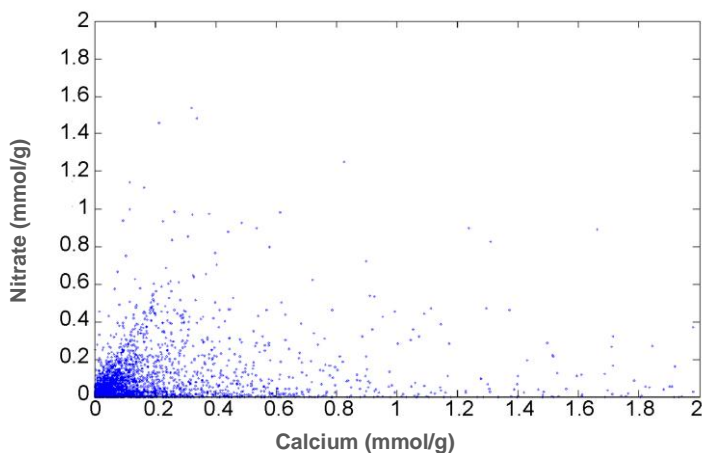
The third approach deals with the average ion concentration found in the plaster and render samples (Figure 6). All of the salts presented in Table 6 with the exception of starkeyite are present in the output. A similar output is derived from the stone samples, however excluding nitratine.



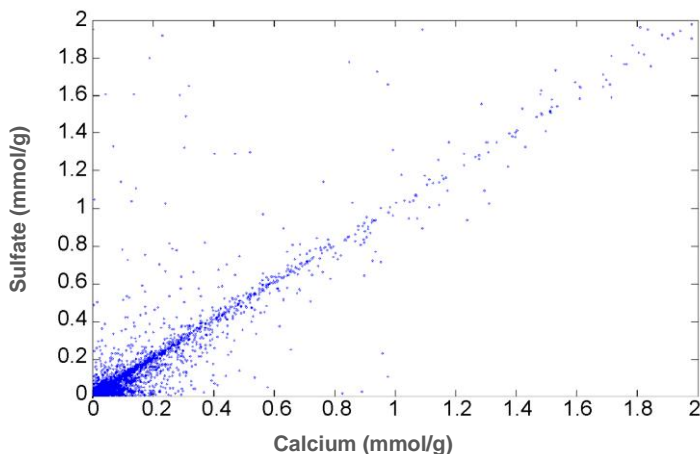
**Figure 6:** ECOS/RUNSALT output (25°C) of the average ion composition of plaster and render samples (table 5), after correction for gypsum.

The data structure further enables the study of the correlation amongst the ions as well, possibly identifying recurrent ion ratios. For example, the

quantities of calcium versus nitrate ions and the calcium versus sulfate ions of all samples are plotted in Figures 7 and 8. Between the calcium and nitrate ions, a spurious correlation can be noticed for a small number of samples and this up to a calcium-concentration of 0.2 mmol/g at a ratio of approximately 1:2 (calcium versus nitrate). A noticeably higher correlation between the sulfate and calcium ions is obtained (Figure 8) from which the omnipresence of gypsum is evidenced.



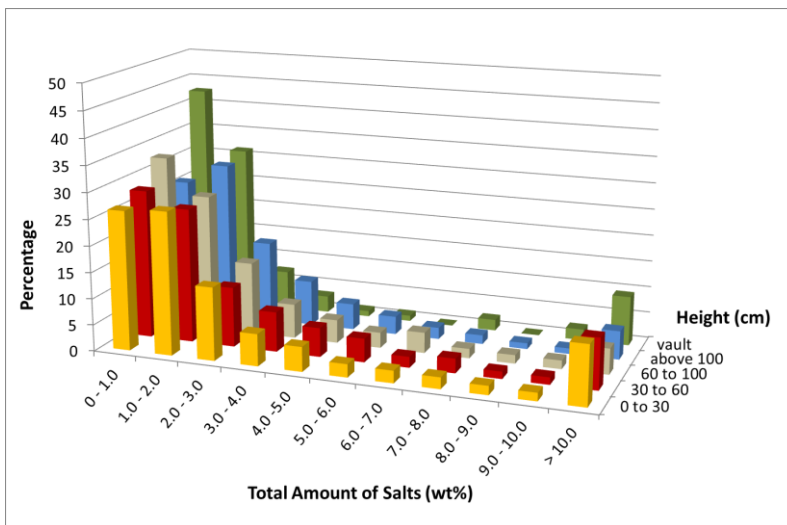
**Figure 7:** Correlation of the amount of calcium versus that of nitrate ions (mmo/gl).



**Figure 8:** Correlation of the amount of calcium and that of sulfate ions (mmol/g).

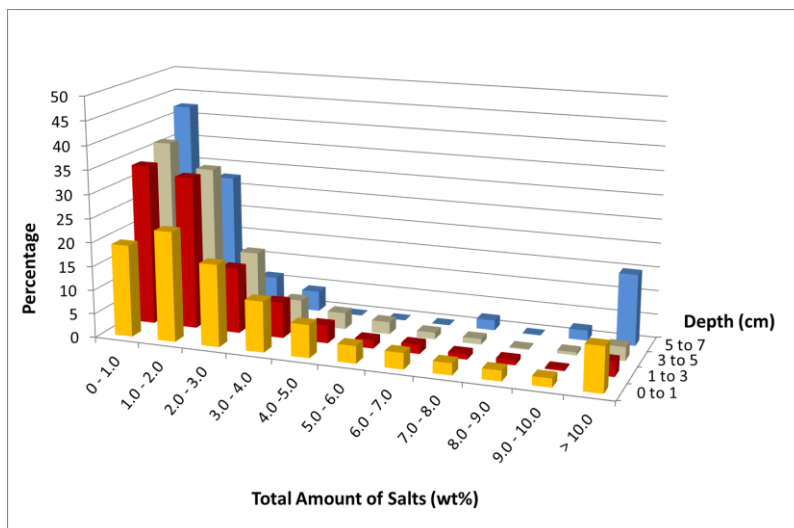
### 5.3 Spatial distribution of salts

The total amount of salts according to the sampling height is plotted in Figure 9. The majority of samples contain, regardless the height, a maximum of 2 wt% of salts. Samples lifted above 1 m contain a higher salt content resulting from rising damp transporting ions to the drying front where salts are deposited. The content in the vaults is generally less when compared to the walls, however a significant amount of samples contain a higher salt content above 10 wt% when compared to samples lifted above 60 cm in the walls.



**Figure 9:** Variation of the total amount of salts, including gypsum, according to the height at which the samples were lifted.

The total amount of salts according to the sampling depth is plotted in Figure 10. Closer to the surface of the material the average amount of salts tends to increase. An exception can be seen at a depth between 5 and 7 cm, where a larger percentage of samples contain a salt concentration above 10 wt%. Naturally, such an evaluation is bias as in normal conditions samples are only lifted up to a depth of 5 cm while drilling samples at a greater depth are only lifted when severe damage or large amounts of efflorescence are visible.



**Figure 10:** Variation of the total amount of salts, including gypsum, according to the sampling depth.

## 6 Conclusions

The presented database has become KIK's main location to collect quantitative ion data of the aqueous extract of powder samples lifted in Belgian monuments. The samples are classified by date, location, material, depth and height. Within the database calculations are automated to aid the interpretation of the salt distribution within the monument, sculpture or archaeological site that is under investigation. Furthermore, it can be used as an educational tool to further the understanding of the complexity of ions and salt mixtures for many conservation practitioners.

Statistical analysis of the data evidences average ion mixtures per material, which can then be interpreted with the ECOS/RUNSALT program to analyze the thermodynamic behavior of the ion mixture. The results show complex mixtures with the presence of kieserite, starkeyite, thenardite, nitratine, niter, darapskite, halite, bloedite and aphanthalite. However the program has its limitations as it excludes gypsum and carbonate salts. It also has a known error relating to the magnesium sulfates, as hexahydrite is not shown in the output. Hexahydrite is however the most likely reaction product with increasing RH [3, 4]. Additionally, the formation and deterioration potential of the double salts darapskite, aphanthalite and bloedite can be questioned when in the presence of other salts or within different porous materials [3, 5].

The main goal of the database is to generate average salt mixtures found in the different materials according to various criteria such as the geographic region, the type of building material, the depth and the height to narrow down specific research needs and to move from single salts to relevant complex mixtures. Ultimately the location data will be linked to a geographic information system (GIS) and the database will be made available online such that other research institutions can add data to further increase the relevancy of the database.

## **References**

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