

Article

# The Ultramicrochemical Analyses (UMCA) of Fluid Inclusions in Halite and Experimental Research to Improve the Accuracy of Measurement

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**Abstract:** Fluid inclusions in halite are widely used in research to determine the conditions of sedimentation in salt basins and reconstruct the chemical composition of seawater during a specific geological period. However, previous preliminary studies of the genetic types of inclusions, considered in the present research project, have not received due attention. Consequently, we decided to take into account the main distinguishing features of fluid inclusions in halite, belonging to various genetic types. The ultramicrochemical analysis (UMCA) method is one of the several methods that are used for the quantitative determination of the chemical composition of the primary fluid inclusions in halite. We have upgraded that technique, and that allowed us to reduce the analytical error rates of each component determination. The error rates were calculated in the study of Ca-rich and SO<sub>4</sub>-rich types of natural sedimentary brines.

**Keywords:** halite; fluid inclusions; capillary; UMCA method; analytical error

## 1. Introduction

Fluid inclusions in halite constitute sources of information on the composition of seawater in the ancient oceans, e.g., [1–4], as well as the conditions of mineral crystallization in salt deposits [5–7] and others. Halite, like no other mineral, contains properly diagnosed primary fluid inclusions that characterize the sedimentary environment [8,9].

The average volume of the brine contained in the fluid inclusions of halite is in a range from 0.00n to 0.00000n mm<sup>3</sup>, and such micro quantities of brines exclude the use of any conventional methods of chemical analysis to determine the quantitative chemical composition. The ultramicrochemical method (UMCA) for studying the brines from fluid inclusions in halite was developed at the end of the 1960s by O.I. Petrychenko [10]. Later, other methods of extracted brine microanalysis, using various types of radiation (inductively coupled plasma spectroscopy and ion chromatography), appeared [11]. In the 1980s, B. Lazar and G.D. Holland modernized those methods of analysis and created a high-precision ion-chromatographic method (Extraction-IC) [12]. In the late 1990s and early 2000s, two more methods of quantitative X-ray microanalysis (Cryo-SEM-EDS and ESEM-EDS) were developed [13,14]. Recently, works have been published on the successful use of laser ablation inductively coupled plasma mass spectrometry (the LA-ICP-MS method) for the study of brines from fluid inclusions in halite [15–17].

The UMCA method differs from other similar techniques by the simplicity of methodological operations, the speed of obtaining data, and low cost. Until recently, however, its significant drawback

was identified in view of considerable analytical error rates in determining individual components. Since the first application of the UMCA, the methodology has been regularly updated. To reduce the error rate of a single analysis and increase the sensitivity of the method, we have standardized and improved some individual operations as well.

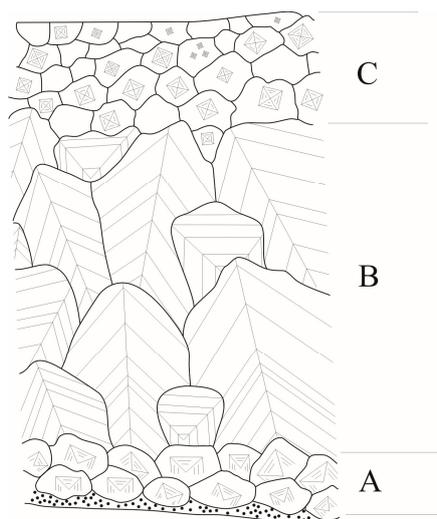
The purpose of this article is to present our upgraded UMCA method and experimental research to improve methodological techniques and the accuracy of a single measurement. We provide here sample analyses of the Middle Miocene (Badenian) halite, in the context of the preselection of fluid inclusions, for a correct interpretation of the data obtained.

## 2. Fluid Inclusions in Halite

Depending on the genetic type of fluid inclusion, the chemical composition data allow us to characterize either the sedimentation or the post-sedimentation environment. Fluid inclusions of two genetic types are distinguished in halite: primary and secondary [18–20].

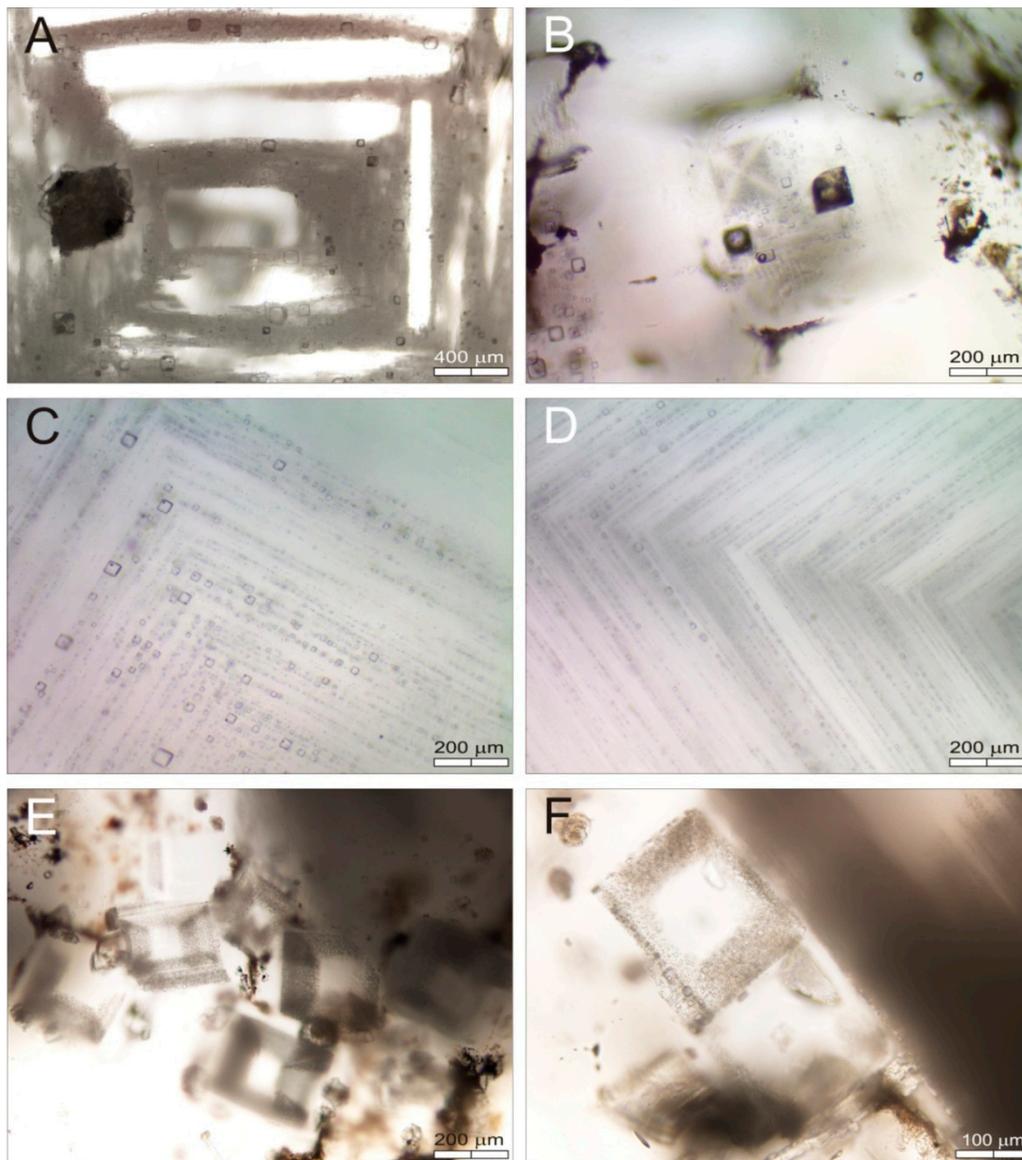
### 2.1. Primary Inclusions

Sedimentary halite is formed either at the bottom of the salt basin (chevron halite) or on the surface of brine (cumulate halite) and at the zone of mixing brines of different composition (salting-out halite) (Figures 1 and 2). There is a genetic relationship between those two different types of halite, and that issue was clarified during the study of modern salt lakes [21,22].



**Figure 1.** Sedimentation differences of halite in the context of salt deposits [8]. (A) fine-grained salt with relics of near-surface precipitating halite (cumulate halite). (B) coarse and medium-grained salt with the remnants of bottom grown halite (chevron halite). (C) fine-grained salt with the relics of salting-out halite. Chevron halite (“outlined” by primary fluid inclusions) is the main and the most common form of sedimentary halite in ancient salt deposits. Other types of sedimentary halite are quite rare.

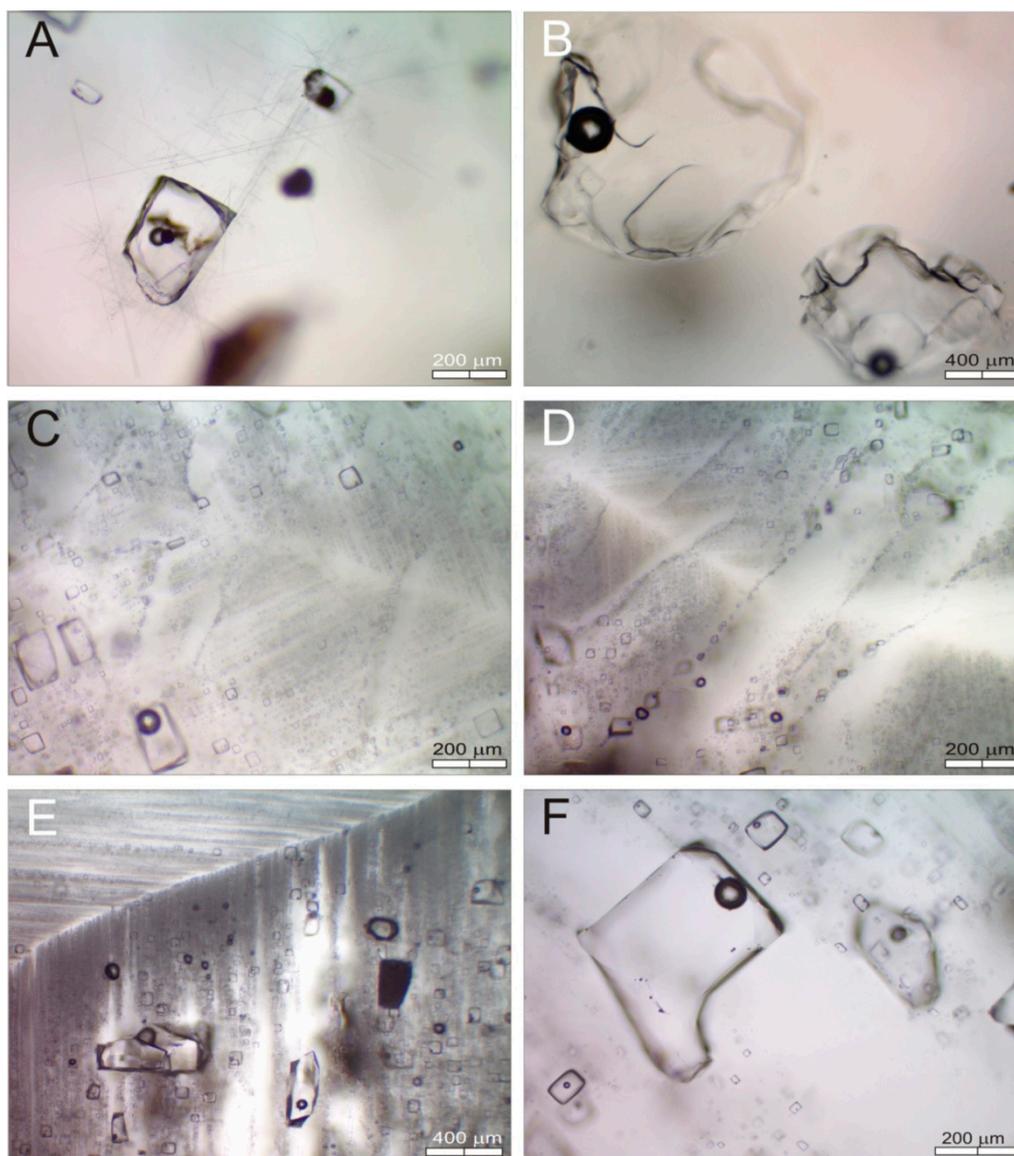
The formation of skeletal cubic halite nuclei (salting-out halite) occurs in the basins whose solutions have reached the stage of potash-salt precipitation and where there is a constant influx of fresh seawater, with relatively low density. Thus, typical brine stratification conditions occur. During the process of mixing the solutions of various concentrations, crystallization of halite begins without additional evaporation, and skeletal cubes of halite crystals are formed. Primary inclusions, in the form of negative cubic crystals, are located along the mineral growth zones and are identified in microscopic studies (Figure 2). A completely preserved sedimentary texture of halite is not always observed. Sometimes, only some fragments of zones with inclusions are detected in crystals, which makes it difficult to accurately determine their origin.



**Figure 2.** Fluid inclusions in sedimentation textures of halite: (A,B) within cumulate halite ((A)—Upper Kama Basin, Kungurian, sample no. 34/87; (B)—Transcarpathian Basin, Badenian, Well 6-T, depth interval: 1110–1114 m); (C,D) within chevron halite ((C)—Transcarpathian Basin, Badenian, sample no. H-III-70; (D)—Transcarpathian Basin, Badenian, Well 6-T, depth interval: 1145–1149 m); (E,F) within salting-out halite (Upper Pechora Basin, Kungurian, sample no. 3/14).

## 2.2. Secondary Inclusions

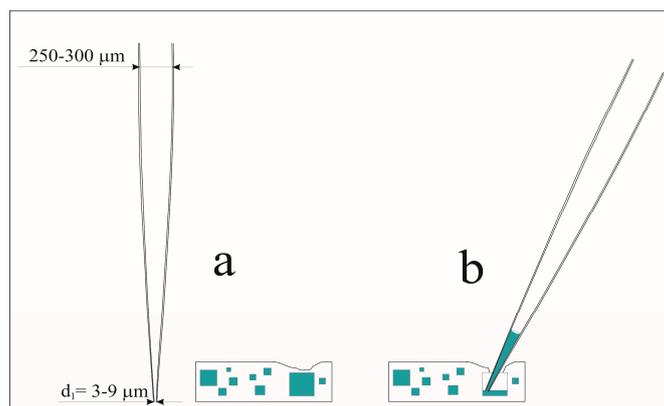
Inclusions of this type involve negative crystals of various, often-irregular shapes, located along cracks in transparent halite (Figure 3A,B). Such inclusions are also found in sedimentary halite, next to primary inclusions. As a rule, they differ from the primary ones by increased internal pressure and increased gas saturation within brine. They can also be identified, owing to their presence within the transparent parts of crystals or the secant cracks in chevron halite (Figure 3C–F). However, the difference between the secondary and primary inclusions is not always noticeable visually. If that is the case, the genetic type of inclusion can be precisely determined only by the study of the chemical composition of respective brines.



**Figure 3.** Secondary fluid inclusions. (A) fluid inclusions within transparent recrystallized halite from the Forecarpathian Basin, Badenian, sample no. H-III-70; (B) from the Ordos Basin, Ordovician, Well K-1, depth: 2385.5 m; (C–F) secondary fluid inclusions within sedimentary halite from the Transcarpathian Basin, Badenian, Well 6-T, interval depths: (C)—1075–1078 m; (D)—1168–1179 m; (E,F) 1087–1090 m.

### 3. Description of the UMCA Method

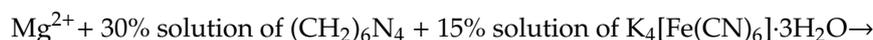
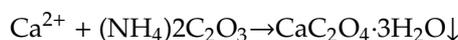
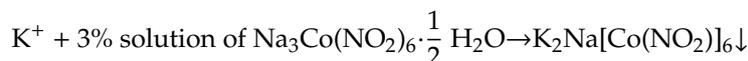
The ultramicrochemical method of the fluid inclusion analysis (UMCA) allows us to determine the main components of brines, such as  $K^+$ ,  $SO_4^{2-}$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  [10]. That method concerns the quantitative determination of ions in a solution, based on the volume of the obtained precipitate salt [23]. Reactions are carried out in fitted capillaries, which are glass tubes with a diameter of 200–250  $\mu m$ , with a conical end. The diameter of the inlet of the capillary cone ( $d_1$ ) is 4–9  $\mu m$  (Figure 4). The determination time of one component in brine (from the extraction of brine to the measurement of the precipitate) is less than 20 min. For the precipitation of individual microelements from the inclusion's brines, compounds that interact with only this one specific component are used. Products of these reactions form fine- and medium-grained precipitates, with smooth contours.



**Figure 4.** Initial operations of UMCA: (a) halite is washed above the selected inclusion; (b) extraction of brine with a glass capillary.

The potassium ion is precipitated with a 2–5% solution of  $\text{Na}_3\text{Co}(\text{NO}_2)_6 \cdot \frac{1}{2} \text{H}_2\text{O}$ . The sulfate ion with a 30% solution of  $\text{BaCl}_2$ ; calcium with a 5% solution of  $(\text{NH}_4)_2\text{C}_2\text{O}_3$ , and magnesium (if the content of  $\text{Ca}^{2+}$  in the analyzed brine is 0–6 g/L), unequal parts of a 30% solution of  $(\text{CH}_2)_6\text{N}_4$ , and a 15% solution of  $\text{K}_4\text{Fe}[(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ . If the content of  $\text{Ca}^{2+}$  in the analyzed brine is >6g/L, the magnesium ion is determined by the reagent mentioned above (a 30% solution of urotropine + a 15% solution of  $\text{K}_4\text{Fe}[(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ ), but only after the precipitation of  $\text{Ca}^{2+}$  and removal of its salt precipitate from the capillary (by cutting off the end of the capillary, with sediment in a drop of reaction on  $\text{Mg}^{2+}$ ).

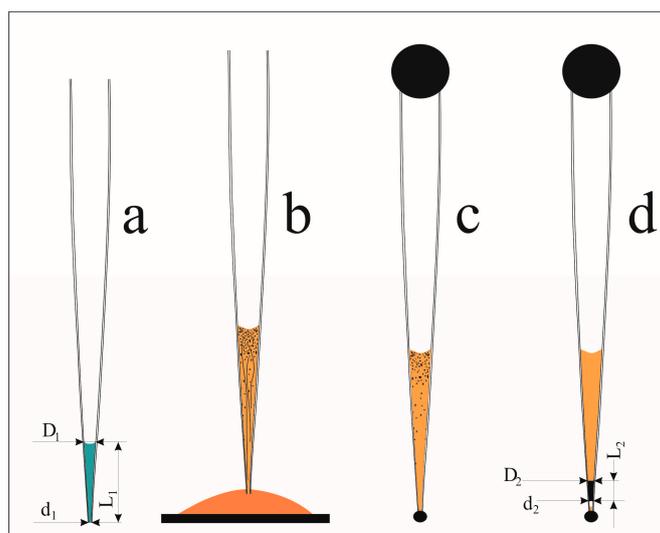
The process of the precipitation of salts of the main components takes place under the following reactions [23]:



The error rates of single determinations by the UMCA method of each of the main ions in fluid inclusion are different. For  $\text{K}^+$ , the error rate is 23%, for  $\text{SO}_4^{2-}$ —38%, for  $\text{Ca}^{2+}$ —43%, and for  $\text{Mg}^{2+}$ —21%. When investigating the  $\text{Mg}^{2+}$  ion in a Ca-rich brine, the analytical error rate doubles. To reduce the error rate to 10–17%, it is necessary to carry out two or three parallel analyses. The minimum concentrations of each ion that can be determined are the following: 0.8 g/L for  $\text{K}^+$ , 0.5 g/L for  $\text{SO}_4^{2-}$ , 0.9 g/L, for  $\text{Ca}^{2+}$ , and 1.0 g/L for  $\text{Mg}^{2+}$ , respectively.

All our operations were carried out under an optical microscope. The halite surface was dissolved by a thin stream of water above the selected fluid inclusion. The distance left to inclusion was 10–20  $\mu\text{m}$  (Figure 4a). Then, the surface of halite was dried and pierced with a fine steel needle; and immediately (4–5 s) afterward, the brine from the inclusion was extracted with a capillary (Figure 4b).

Brine can be extracted to 1–3 capillaries (depending on the diameter of the end of the capillaries) from a single fluid inclusion of the size of 70–100  $\mu\text{m}$ . After extraction, the brine volume is determined (Figure 5a). The corresponding reagent is introduced into the capillary (Figure 5b), the ends of the capillary are sealed (Figure 5c), and the capillary is centrifuged (at 8000 rpm for 15 min). Finally, the volume of the obtained precipitate (Figure 5d) is compared to the precipitate volume of a standard brine sample.

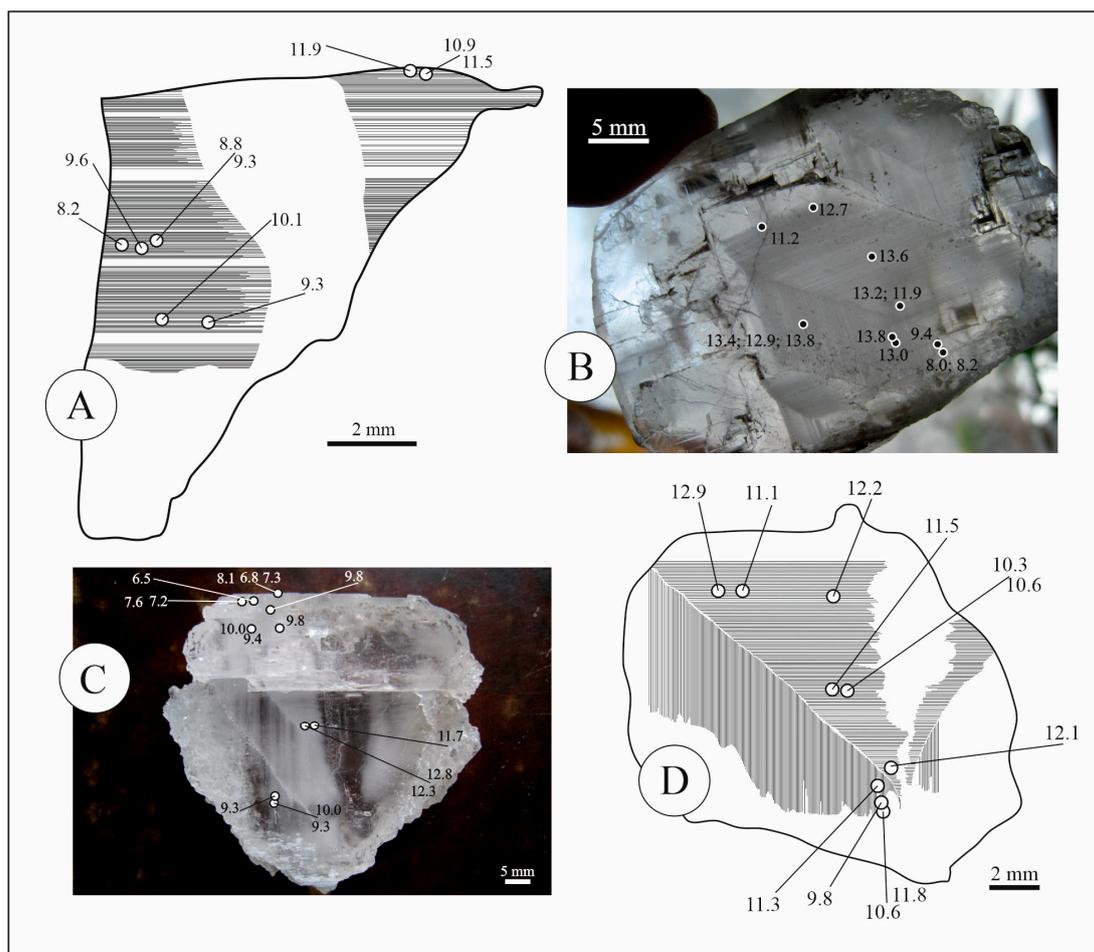


**Figure 5.** The final operations of UMCA: (a) determination of the volume of brine;(b) a reagent kit for the precipitation of the corresponding component; (c) sealing of the capillary; (d) determination of the precipitate volume.

#### 4. UMCA Method Upgrade and Estimation of the Analytical Error Rates

Compared to other methods, the results obtained by the UMCA method were either overestimated or underestimated, with respect to the correct primary values. That was due to the insufficient accuracy of the determination of the volume of brine collected in the capillary, and the heterogeneity of the precipitate obtained in individual cases. During our experimental studies, the effects of those and other factors were partially eliminated, owing to the standardization of capillary fitting and improvement of capillary operations. A test utilizing blanks, e.g., in synthetic halite-hosted fluid inclusions, was not implemented in this study, and errors were calculated via the method presented in [10] with the use of artificial brines. The UMCA method upgrade included the following:

1. The inclusion opening operation was carried out in a special chamber, with high humidity, to prevent evaporation of the low-concentration brine.
2. For each of the components being determined, capillaries of various standard shapes were used, with a known diameter of a conical end; consequently, the time to determine the volume of the brine was reduced, and evaporation was decreased as well.
3. In the cases of low contents of the components analyzed in brine ( $<1$  g/L), we used the capillaries with a minimum inlet diameter.
4. To reduce precipitation time of each component by the reagent, and thus, to obtain a uniform fine-grained precipitate, the value of  $L_1$  in a capillary (Figure 6A), with the inlet diameter of  $9\text{--}10\ \mu\text{m}$ , did not exceed  $2.5\ \text{mm}$ , and, in the case of a capillary with the inlet diameter of  $4\text{--}5\ \mu\text{m}$ , did not exceed by more than  $1.5\ \text{mm}$ ; the amount of collected brine was easily controlled under a microscope.
5. Brine was stirred in a closed capillary as a result of exposure to hot steel needle; owing to brine movements, the particles of sediment adhering to its walls were removed; thus, we obtained compact precipitate after centrifugation.



**Figure 6.** Chevron halite crystals from the Badenian Forecarpathian Basin. Dots show the locations of the investigated primary fluid inclusions, with the  $K^+$  contents within the halite; plate numbers correspond to those in Table 2. (A) Drawing of chevron halite from the Forecarpathian Basin, Ukraine. Well Hrynivka 525, depth 422 m, sample, no. 1358. (B) Chevron halite crystal from Forecarpathian Basin, Poland. Wieliczka Salt Mine, sample from boulder of the Laminated Green Salt. (C) Fragment of halite chevron crystal from Spiza Salts series, Wieliczka Salt Mine. (D) Drawing zonation of chevron halite from Shaft Salt layer, Wieliczka Salt Mine.

To reduce the error rate of a single determination, we carried out control analyses regarding K, Mg, and  $SO_4$  (or Ca) of artificial brines, with a known concentration of those components, before each series of analyses for reconstructing the chemical composition of the brines from an individual basin. We obtained close indicators, with minimum error rates. Why did we decide on UMCA testing with artificial brines before each series of fluid inclusion brine analyses? We had studied natural brines at various times of the year and various temperatures, and found that the reactions developed each time differently. The ideal conditions were identified at 20–22 °C of average humidity. Then, the reaction was complete and quick, and the precipitate was fine-grained, with good precipitation in the narrow end of the capillary. Evaporation from the open inclusion and the capillary was insignificant. That process was crucial for conducting analyses under the UMCA method.

Of course, it is challenging to make an entirely identical solution in natural conditions. Natural brine represents certain pH and Eh values; in addition to K, Mg,  $SO_4$  and Ca, there are certain amounts of  $CO_3$ , and various other trace elements identified. Therefore, the result of the natural brine analysis was somewhat affected by those additional factors that affected a single determination error rate.

The error rate of a single analysis under the upgraded UMCA method was calculated based on the study of Ca-rich and  $SO_4$ -rich genetic types of natural sedimentary brines (Table 1). The error rates

were calculated in such a way that all the primary inclusions from the same zone of chevron halite were analyzed, and thus, the chemical composition of sedimentary brines was the same. The figures might be somewhat different in other zones. The  $K^+$  ion content was determined in several inclusions, followed by the calculation of the average value. Depending on that average value, the error rate of a single determination of the potassium ion content was calculated. The error rates in the determinations of  $Mg^{2+}$  and  $SO_4^{2-}$  (or  $Ca^{2+}$  into Na-K-Mg-Ca-Cl (Ca-rich) type) were calculated in the same way.

**Table 1.** Analytical error rates under the ultramicrochemical analyses (UMCA) method before and after method upgrading, calculated for the analyses of the main components in Ca-rich and  $SO_4$ -rich brines. The error rates were calculated under the upgraded UMCA method, in respect of the data obtained from the sedimentary brine studies. The primary inclusions located strictly along separate zones of the bottom chevron halite crystals had been tested previously. Halite samples come from the Ordovician salt of the Ordos Basin [4], and also from the Cretaceous salt deposits of the Sakon Nakhon Basin (Laos) and the Badenian salt deposit from Poland (unpublished data).

Type of Brine	The Error Rate of Analysis, %			
	$K^+$	$Mg^{2+}$	$SO_4^{2-}$	$Ca^{2+}$
	<b>Standard UMCA method</b>			
$SO_4$ -rich	23	21	38	–
Ca-rich		42	–	43
	<b>Upgraded UMCA method</b>			
$SO_4$ -rich	1–24	1–6	2–8	–
Ca-rich		1–19	–	1–26

It should be noted that it was possible to calculate the error rate of a single analysis in that way only for bottom-growth chevron halite crystals (Figure 1B; Table 1). We were unable to do such a study of the error rate on the primary inclusions in the cumulate halite (Figure 1A). In the cumulate halite, even that found in the adjacent primary inclusions, the concentrations of the components may differ. However, the ratios between the components remain constant.

Primary fluid inclusions in skeletal cubic halite nuclei (salting-out halite) cannot be investigated, owing to their small sizes (less than 20  $\mu m$ ). In the secondary inclusion brines, not only did a different ratio between the main components occur, but those could also even represent various chemical types.

## 5. Studies of the Inclusions in Individual Chevron Halite from Various Zones under the UMCA Method

A sufficient number of primary inclusions of chevron halite, larger than 40  $\mu m$  each, allowed us to test the upgraded UMCA method, using natural brines. The study of the inclusions in individual bottom halite crystals from different zones produce microscale information about the conditions and progress of the salt accumulation process in the basin. However, the mechanism of formation of that type of halite should be first considered.

Chevron halite samples from the Middle Miocene (Badenian) salts from the Carpathian Foredeep (Hrynivka 525 well in Ukraine and Wieliczka Salt Mine in Poland) were used for the tests (Figure 6). Geochemical studies indicated that Badenian seawater in the Forecarpathian Basin was the primary source of salts [24–26]. However, the amount and share of continental water inflow to the basin were controversial and discussed, e.g., [27,28]. This influx did not significantly affect the change in the ratio between the main ions in the basin brine [29–32]; however, some changes in the content of magnesium and sulfate ion in brine might depend on the intensity of the continental run-off [6,26]. Therefore, the content of potassium ion was the main indicator of increase or decrease in concentration of brine (Table 2; Figure 6).

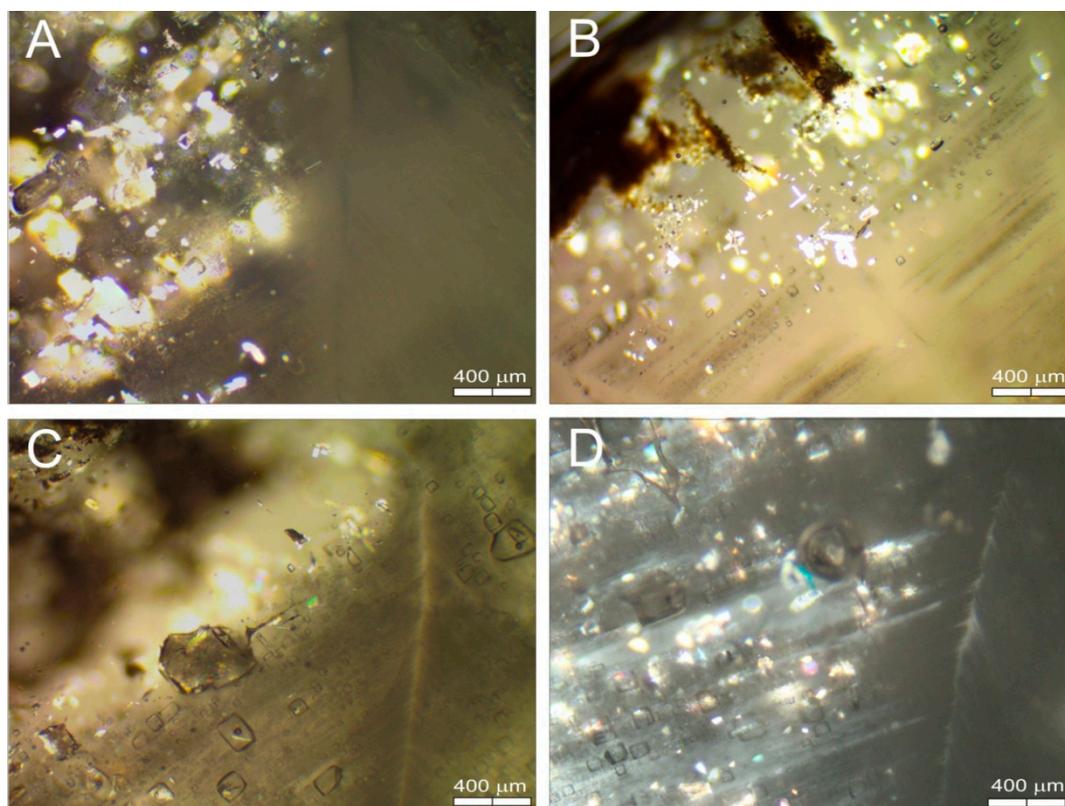
**Table 2.** The analytical error rate under the upgraded UMCA method, for a single determination of the K<sup>+</sup> content in the SO<sub>4</sub>-rich type of brine. Due to a small number of analyses (<10), errors were calculated via Student's t-distribution. The chemical composition of sedimentary brine was studied based on the chevron halite inclusions from the Forecarpathian Basin (Well Hrynivka 525 and the Wieliczka Salt Mine).

No.at Figure 7	The Distance of Studied Zone from the Base of the Chevron (mm)	Concentration Ion K <sup>+</sup> [g/L] (Mean Value in the Parentheses)	Analytical Error (%)
Well Hrynivka 525, depth 422 m, sample no. 1358			
A	6.5	11.9; 11.2 (11.6)	3–4
	3	8.2; 9.6; 9.1 (9.0)	7–9
	1	10.1; 9.3 (8.9)	5–13
The Wieliczka Salt Mine			
Laminated Green Salt			
B	19.6	11.2; 12.7 (12.0)	6–7
	12.2	13.4; 13.6 (13.5)	1
	6.7	12.6; 13.0; 13.8 (13.0)	3–6
	1.6–2	9.4; 8.0; 8.2 (8.2)	2–14
Spiza Salt			
C	22.5–23.5	7.4; 6.5; 7.4 (7.1)	4–8
	21	9.8 (9.8)	–
	17	9.7; 9.8 (9.8)	1
	6.5	9.7; 9.3 (9.5)	2
	1.5	11.7; 12.6 (12.2)	3–4
Shaft Salt			
D	7.5	12.9; 11.1; 12.2 (12.1)	7–8
	4.5	11.5; 10.5 (11.0)	5
	1.7	11.2; 9.8; 11.3; 12.1 (11.1)	9–12

It was established that during the growth of individual halite crystals, the conditions of salt sedimentation were quite variable. The concentration of bottom brine either increased, or decreased, or remained unchanged (Table 2; Figure 6). Several factors contributed to that issue, namely:

1. Water exchange irregularities in the salt basin, due to intense evaporation and changes in salinity (Figure 6A,B).
2. Redeposition of salt, evidenced by a decrease in the concentration of brine during halite crystallization (Figure 6C). That was caused by the inflows of less concentrated waters (although saturated with NaCl). Redeposition of halite occurred under seawater deprived of a significant portion of Ca(HCO<sub>3</sub>)<sub>2</sub>, previously precipitated earlier in calcium carbonates and calcium sulfates in the outer sections of the evaporating basin. In the case of our analyzed sample of Spiza salt from the Wieliczka Salt Mine (Figure 6C), brines of various concentrations had to be rapidly mixed, because there were no indications of disruption during the growth of chevron halite. Consequently, based on the assumption of salt redeposition with the occurrence of salt conglomerates [26,33], a low bromine content in the Badenian halite was confirmed [25,34,35]. The inflow of freshwater into the salt basin is also evidenced by the presence of a significant amount of calcium sulfate crystals in the sedimentary halite and in the primary fluid inclusions in the halite (Figure 7). Sulfate crystals were found in significant quantities in the zones where chevron halite was formed at the boundary of the layers; this is where physical and chemical conditions had been favorable.
3. Brine stratification into two layers that were not mixed by convection occurred, e.g., [36]. An example of this type of physical and chemical conditions in the salt basin was represented by an irregular zonation in halite from Shaft Salt of the Wieliczka Salt Mine (Figure 6D). In brine stratification, the bottom layer was more concentrated and denser than the top one (due to the

presence of magnesium chloride), and both layers were saturated with NaCl. Such conditions were caused, that during the growth of halite crystals at the bottom, the potassium concentration remained unchanged in brine inclusions.



**Figure 7.** Small crystals of calcium sulfate in sedimentary halite (high interference colors in crossed polars). Crystals in halite are represented by anhydrite, and within fluid inclusions by gypsum, bassanite, and anhydrite [37]. (A–C)—Transcarpathian Basin, Badenian, Mukachevo, Well 6-T, depth interval: (A)—1047–1050 m; (B)—1314–1318 m; (C)—1047–1050 m; (D)—Transcarpathian Basin, Badenian, Solotvyno Salt Mine, sample no. 29.

## 6. Discussion and Conclusions

The fundamental differences existing between the currently-used methods of the quantitative determination of the chemical composition of brines, collected from fluid inclusions of halite, involve the complexity of methodological operations. The accuracy of the determinations of the main components ( $K^+$ ,  $SO_4^{2-}$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ ) is estimated at 3–21% for these methods: Cryo-SEM-EDS, ESEM-EDS, and LA-ICP-MS, and at up to 25% for the UMCA method. The minimum size of inclusion that is suitable for analysis is 10–20  $\mu m$  for the Cryo-SEM-EDS, ESEM-EDS, and LA-ICP-MS methods, and more than 40  $\mu m$  for the UMCA method. However, the results of the analyses of halite inclusion brine of the same samples, although obtained by various methods, did not always comply with each other. That was caused by the fact that the analyses concerned the inclusions of various genetic types, occurring within one primary texture, or the study of inclusions concerned chevron halite collected from multiple different zones.

Since not all the inclusions of sedimentary halite were distinctly primary, the ratios of ions in the brine of primary inclusions may have varied within different zones of the same chevron texture. Consequently, it was necessary not only to determine the type of texture, but also to pre-identify the types of inclusions [32,38,39]. The comparisons of the results relating to the inclusion brine composition, obtained by various methods (UMCA, Cryo-SEM-EDS, and ESEM-EDS), applied to the same group of

samples, indicated that all data were comparable, provided that the genetic type of fluid inclusion was exact [40]. In that regard (i.e., a precise preliminary determination of the genetic type of inclusions), the UMCA method had a significant advantage, since it allowed us to estimate the pressure inside the inclusion and the gas content in brines by observing the inclusion reactions during inclusion opening.

A considerable drawback of the UMCA method, until recently, consisted of low analytical accuracy of a single determination of each of the components (see Table 1). By eliminating the errors that led to the dispersion of the analytical results, we achieved an acceptable accuracy of a single determination. Therefore, we significantly increased the upgraded method's competitiveness, concerning the other techniques applied to the investigations of the chemical compositions of halite inclusion brines.

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