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Photometric Determination of Trace Amounts of Aluminum in Nearly Saturated Rock Salt Solutions Used by Chlor-alkali Industry

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Abstract

The previously widespread mercury cell technology in chlorine production has now been replaced by more environmentally friendly membrane cell electrolysis which is a Best Available Techniques (BAT) technology. However, this requires a much cleaner brine containing contaminants (Al, Ca, Mg, etc.) in the order of ng/g at most. For this reason, it's very important to detect trace amounts of aluminum in concentrated saline media in the simplest and fastest way. To the best of our knowledge, no one has previously developed a spectrophotometric method capable of detecting aluminum in ionic forms selectively in the order of ng/g in concentrated saline media, without any preconcentration or separation step. Our advanced analytical method provides an opportunity for this. During the analytical procedure, a colored complex ion is formed from the dissolved aluminum content of the sample with eriochrome cyanine R (ECR) ligand in buffered pH medium. The sensitivity of the measurement is increased by adding quaternary ammonium salt. The colored complex ion is formed in 15 minutes, then the absorbance measurement can be performed for 90 minutes. The effect of rock salt interference was eliminated by proper calibration. In our work the dependence of the signal on temperature, pH, time elapsed after the addition of reactants, the dosing sequence, the salinity of the medium was examined, furthermore, we studied which wavelength-absorbance values give the best fit (highest R^2 value) and the highest sensitivity in case of linear calibration. Surprisingly, increasing the salinity significantly improves the sensitivity of the measurement.

Keywords

photochemistry, measurement, aluminum, microscale, chlor-alkali industry

1 Introduction

Determination of trace amounts of aluminum (in the order of ng/g) is a necessary need in many fields of science, industry and medicine, in various matrices [1–5]. Trace amounts of aluminum are of paramount importance in the chemical industry, especially in the field of membrane cell chlorine production [4, 5]. Medicine classifies aluminum as a substance that is toxic to the human body because it can be linked to dementia, Alzheimer's disease, and kidney failure, among others [6–8]. The European Commission has ordered that diluted dialysis fluids must not contain more than 10 μg/l of aluminum and limit values also apply to cosmetics and drinking water (200 μg/l – WHO) [9–11].

The determination of trace amounts of aluminum in a concentrated NaCl-containing medium is a common task in membrane cell rock salt electrolysis, which is the BAT (Best Available Techniques) technology for chlorine production [12]. This technology replaced the previously widespread mercury cell electrolysis, which had to be phased out in the signatory countries under the Minamata Convention (128 countries, 2022), which was established in 2013 and entered into force in 2017 [13, 14]. However, membrane cell rock salt electrolysis requires a very high purity rock salt solution, as certain metal contaminants (especially aluminum), even at concentrations below μg/g, severely damage the membrane of the electrolysis cell which reduces the prescribed service life of the membrane by several years and also leads to higher operating costs due to the increase in electricity consumption [15]. For this reason, the advantageous recycling of saline technological waters from the principle of sustainability and economy

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also requires special attention and continuous monitoring of the aluminum content [4, 5]. Sustainability, cleaner production [16], reduction of water consumption and as much water recycling as possible [17] are very important in today's chemical industry. Therefore, the determination of the aluminum content in trace amounts, which is as simple, fast and cheap as possible, is of paramount importance for the chemical industry, as the present problem arises in connection with the production of basic raw materials: chlorine, hydrogen and caustic soda. These raw materials are used to produce many chemical products [18–22].

Although methods for the trace determination of aluminum have been known so far, they can usually be performed with equipment requiring high investment costs – for example graphite furnace atomic absorption spectroscopy (GF-AAS), nuclear magnetic resonance spectroscopy (NMR) and inductively coupled plasma atomic emission, optical emission or mass spectroscopy, (ICP-AES, ICP-OES, ICP-MS). These methods are accepted reference methods for the determination of aluminum [23–25]. Compared to the previous methods, electrochemical methods such as electrogravimetry, coulometry, polarography and voltammetry typically have lower selectivity and sensitivity [24–27].

Due to the advantages of spectrophotometric methods, such as their generally good accuracy and precision, ease of operation and relative inexpensiveness, a number of spectrophotometric methods have been developed in the past for the determination of aluminum [27, 28]. These methods typically use a variety of complexing agents. Such widely used reagents are xylenol orange [29], stilbazo [30], chlorophosphonazo I [28], pyrocatechol violet [31], ferron [32], purpurin [33], quinalizarin [34], thymol blue [35] and methylthymol blue [28]. Other color complexing agents used include alizarin red-S [27, 36, 37], chromazol KS [38], semimethylxylenol blue [39], hydroxynaphtol blue [40], bromopyrogallol red [41, 42], indigo carmine [43], gallocyanine [44], calmagite [45], oxin [46], quercetin [47], chrome azurol S [48–51] and morin [52]. These organic dyes form highly colored complexes with aluminum or colloidal aluminum hydroxide [53]. Most of these reactants do not give outstanding sensitivity, in contrast to the eriochrome cyanine R (ECR) reagent, which provides a molar absorption coefficient of 6.5×10^4 L/(mol cm). This value can be further increased up to 1.19×10^5 L/(mol cm) in dilute solutions by the addition of cationic surfactants. Surfactants are preferred in some analytical assays because the spectral properties of the metal ion ligand complex can be favorably affected by the association of surfactants. Based on this, the use of a surfactant to increase sensitivity is definitely justified. However, in the case of measurement with the ECR reagent, different ions, such as Cu(II), Fe(III), Mn(II) and F^-, can have a disturbing interference effect, but these effects can be eliminated with suitable masking agents [26, 27, 54–56].

In the present work, the photometric determination of trace amounts of aluminum is investigated using the ECR complexing reagent and CTAB (cetyltrimethylammonium bromide) cationic surfactant, in a saturated NaCl-containing matrix corresponding to the medium used in membrane cell electrolysis. Similar method was not previously described as suitable for measurement in concentrated salt solution. The work of Shokrollahi et al. [26] examined a method only in dilute medium (pH = 5, room temperature), up to 500-fold molar ratio of Na^+/Al^{3+} and Cl^-/Al^{3+}. This means a NaCl content of less than 0.1 w%, considering the measuring range given for aluminum, in contrast the concentration of the saturated NaCl solution at 25 °C is 26.4 w%. Some other researchers published methods partly based on spectrophotometry for matrices with a higher salt content. However, these methods were also applied to solutions diluter than the nearly saturated brine solution used in the chlor-alkali industry, and various pre-concentration and separation steps were used before the spectrophotometric determination, which make the analysis more complicated and, in some cases, slower [57, 58]. The aim of our work was to develop a method for the photometric determination of trace aluminum in a concentrated saline medium. In addition, we aimed to determine the most favorable conditions in order to achieve the best possible sensitivity, accuracy and precision. Furthermore, we also kept in mind the simplest possible feasibility.

2 Experimental

2.1 Apparates

Absorbance was detected with a Analytikjena Specord® 210 Plus ultraviolet-visible (UV-Vis) spectrophotometer. The pH and temperature measurements were performed with a Mettler Toledo FiveEasy instrument. The reference measurements were made with an ICP-OES device of type Spectro Arcos II. The weights were measured with a Sartorius Quintix224 - 1 CEU balance (0.0001 g accuracy).

2.2 Chemicals

All chemicals used, such as ECR, NaCl, solid aluminum, cetyltrimethylammonium bromide (CTAB), HCl, NaOH, acetic acid and sodium acetate, were provided to us by VWR International.

2.3 Preparation of standard solutions

Stock solutions with an aluminum content of approximately 0.1 wt% were prepared by dissolving analytical grade solid aluminum in hydrochloric acid. The standard solutions with concentrations below µg/g for the validation of the developed method and for the calibrations were prepared by diluting this stock solution using NaCl solution or water. This meant a more than 1000-fold dilution in all cases, so the matrix was given by NaCl solution (or water) used in more than 99.9 w%. The effect of the minimally different matrix resulting from the different weighed amounts of stock solution was neglected. Although, working with glass devices did not significantly affect the aluminum content via either adsorption or desorption based on our investigation, for safety reasons we worked with plastic devices [53].

2.4 Preparation of buffer-surfactant solution

Buffer-surfactant solutions were prepared by weighing the solid reactants, and subsequently dissolving in distilled water. During the preparation, the obtained pH value was checked by measurements. Pure, anhydrous acetic acid, $CH_3COONa \cdot 3\ H_2O$ salt, and anhydrous CTAB were used. During the examination of the effect of pH, the pH of the original sample was modified by the addition of solid sodium hydroxide or cc. hydrochloric acid to ensure that dilution of the samples was negligible and that no previously absent material was introduced into the system.

2.5 The developed measurement method

Afterwards several experiments with the complexing ligands described in the Introduction (Section 1), we concluded that the ECR reagent can be used promisingly in nearly saturated salt solution, after proper developments and modifications in the circumstances. In accordance with the literature, the ECR ligand acts as a bidentate ligand against a number of metal ions, including Al^{3+} ions. Previous studies have shown that the ECR/Al^{3+} molar ratio in the complexes can be maximum 3, however, the species distribution also depends significantly on the pH of the medium used [59–61]. Accordingly, the ECR reagent was used at a concentration of 0.166 mM in the final solution (the absorbance of this solution was measured), in the vicinity of which the detected absorbance did not show a significant dependence on the ECR concentration, so its small fluctuations should not cause substantial errors. The CTAB:ECR molar ratio used was 20:1.

Next, we would like to determine the simplest possible execution of the measurement method. For ease of handling, we intended to use the reagents in the form of assay solution in a favorably high concentration, in order to dilute the sample as little as possible. Unfortunately, it has been found that ECR-CTAB assay solutions begin to degrade after 2 hours, regardless of the storage temperature. However, in our experience, if separate assay solutions are prepared, the ECR assay solution can be stored at room temperature below pH 3 adjusted with acetic acid, while the pH adjustment of the CTAB assay solution is not necessary. According to our examinations, the CTAB can be handled in a solution common to the buffer. Both assay solutions are stable for at least 6 months.

Proper pH control was also required for the measurement, since the pH – as detailed later – significantly affects the absorbance. The pH adjustment with solid reactants is very cumbersome. A sufficiently precise pH adjustment cannot be achieved with concentrated acid or alkaline solutions, and in the case of dilute solutions, the amount of solution to be added depends significantly on the initial pH of the sample, so a new calibration may even become necessary for each sample due to the different matrix (different salinity) based on the different dilution. Using a buffer solution eliminates these problems. In order to keep the dilution ratio as low as possible, it is important to have a high buffer capacity, i.e. a high solubility of the buffer. It is an additional requirement that none of its components react with other substances present or form a precipitate or a more stable complex with aluminum than the Al-ECR complexes. Based on previous work [26, 53], a pH of about 5–6 was expected to be optimal. The lower part of this pH range can be achieved with acetic acid sodium acetate buffer. Of course, for strongly acidic or alkaline solutions, it is recommended to pre-adjust the pH with concentrated hydrochloric acid or solid NaOH.

Based on our findings, the following method is recommended for the determination of trace amounts of aluminum in nearly saturated NaCl solutions:

- Add to the sample an ECR assay solution of 0.08000 w%, adjusted to pH 2.9 with acetic acid, in a weight ratio of 1:6.
- Then add 1:3 by weight of acetic acid sodium acetate-CTAB solution (241.20 g/l CH_3COONa, 26.50 g/l CH_3COOH, 6.10 g/l CTAB) relative to the initial sample to ensure the presence of the surfactant, and the appropriate pH setting to 5.0.

- After 15 to 90 minutes, measure the absorbance of the solution and determine the concentration of the original solution from the previously recorded calibration curve and the dilution ratio.

The scheme of the method is also summarized in Fig. 1, while Fig. 2 shows the spectra of a calibration series.

Our method enables the determination of both the total aluminum content and the aluminum content selectively in dissolved, ionic forms, in contrast to, for example, the ICP-OES measurement, which is only suitable for measuring the total aluminum content. To determine the total aluminum content, the solution to be measured must be acidified below pH 1, heated to 60–70 °C and stirred under these conditions for 1 day. So that the aluminum content, possibly originally present in colloidal or dispersed form, also dissolves, consequently becoming measurable with our developed method. We can selectively measure the dissolved aluminum content by omitting the dissolution procedure described above, since the precipitated aluminum content does not form (in a significant extent) a colored complex with the ECR ligand based on our measurements.

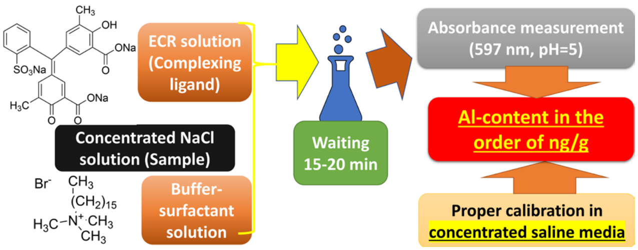

Fig. 1 The scheme of the developed measurement method

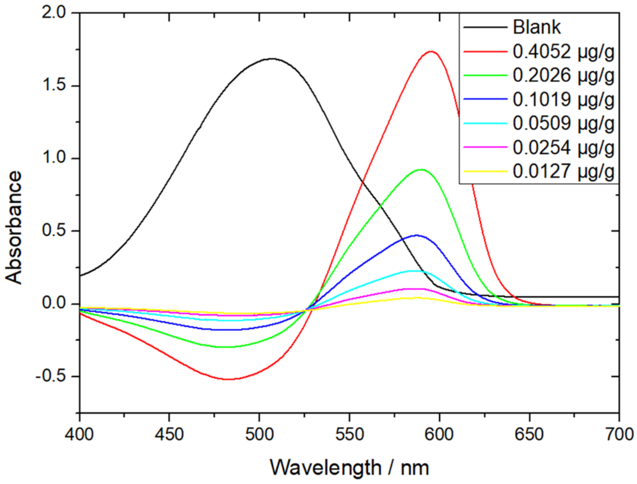

Fig. 2 Spectra of a calibration series compared with blank (concentrated saline medium, 25 °C, pH = 5.0). The legend shows the aluminum content of each solution

This possibility of use is particularly advantageous in certain scientific and industrial measurements.

3 Results and discussion

3.1 Effect of wavelength on precision and accuracy

It was examined at which wavelength the absorbance values obtained give the most accurate calibration, i.e. the calibration line with the highest R^2 coefficient, and how the sensitivity changes with varying the wavelength. The sensitivity is the slope of the calibration line (the absorbance-concentration function), so it's unit is g/µg (the reciprocal of the concentration's unit). The results are shown in Fig. 3 and Fig. 4. In subsequent studies the absorbance values were examined at the wavelengths corresponding to the highest R^2 value, respectively.

Based on Fig. 3 and Fig. 4 it can be stated that the most accurate (highest R^2 coefficient) fitting is obtained at 597 nm in concentrated saline medium at pH 5, while the highest sensitivity is obtained almost at the same, 596 nm.

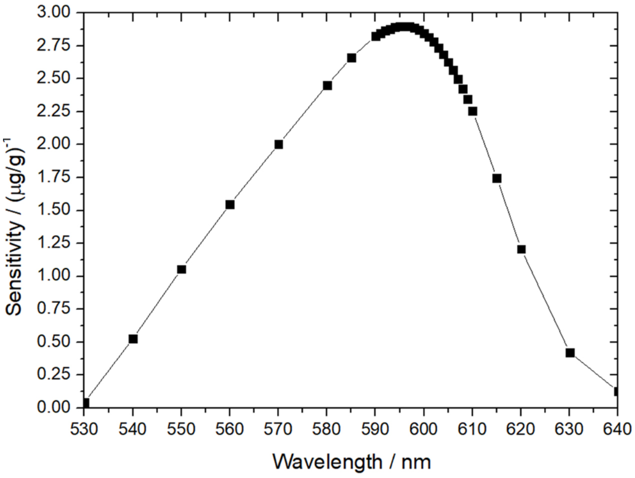

Fig. 3 The effect of wavelength on the sensitivity of the method

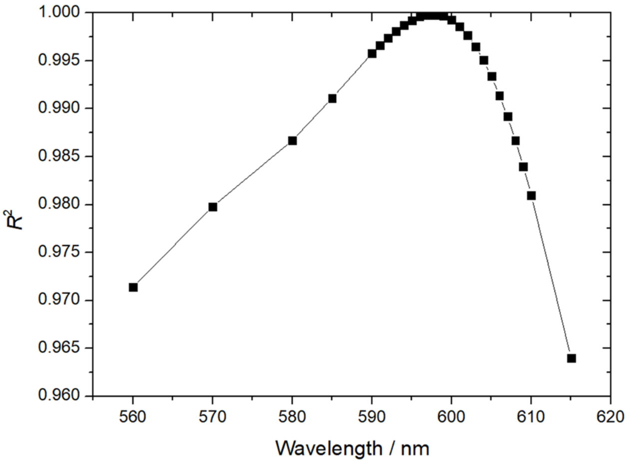

Fig. 4 The effect of wavelength on the R^2 coefficient of the calibration

3.2 Effect of NaCl-content on sensitivity

Calibration series was recorded at different NaCl concentrations (0 w% NaCl – saturated solution) and the parameters of the calibration line achieved from the six-point linear calibration were determined. The absorbance values obtained during the calibration were corrected for the NaCl blank solution of the given concentration. The results are shown in Table 1.

As the salinity increases, the optimal wavelength changes slightly. The coefficients R^2 of the fitted lines are sufficiently high, in all cases above 0.999, which confirms the proper operation of our measurement method. The axial intercepts fluctuate around 0 according to the Lambert-Beer law. Based on the obtained slopes, the interesting and valuable conclusion can be drawn that the sensitivity is improved by the increase of salinity, so the measurement is not only applicable in concentrated saline medium, but its performance significantly exceeds the level for dilute solutions as a consequence of changes in the ionic strength. However, the change in salinity has a significant effect on the measurement, i.e. to perform the measurement properly we need to be aware of the salinity and it is required to use the proper calibration curve. The high R^2 values show that, the measurement can be performed at any salinity.

3.3 Effect of pH on sensitivity

The change in absorbance as a function of pH was examined, while other parameters were not changed. The results obtained are shown in Fig. 5. The signals of the blank and an Al^{3+} solution with a concentration of 180 ng/g were examined and the quadratic curves shown in Fig. 5 were fitted. The pH dependence of the blank-corrected signal was obtained as the difference between the equations of the curves. This procedure was required because the exact measurement pHs differed by a few hundredths in the two cases.

The optimal pH in concentrated saline medium is shifted from 5.0 to 6–6.5 compared to the value described in salt-free medium [26]. However, this pH cannot be adjusted with sufficient buffer capacity using an acetic acid-acetate buffer system. Nevertheless, the measurement also works with satisfactory accuracy, precision and sensitivity in the acetic acid-acetate buffer system, which is one of the cheapest, most widely used buffer systems, accordingly an important advantage is that it does not require special, more expensive buffer systems, such as the relatively inert Good buffers used in the vicinity of the neutral medium [62]. A further advantage of measurement at pH 5 is that, the maximum analytical signal is formed significantly faster compared with at pH 6–7.

Table 1 The effect of salinity on the parameters of the calibration lines

NaCl-content w%	Fit with the highest R^2		Fit with the highest sensitivity	
	Wavelength nm	R^2	Wavelength nm	Sensitivity g/µg
0	603	0.9996	589	1.7424
5	600	0.9997	596	2.2968
10	600	>0.99995	595	2.1751
15	602	0.9998	594	2.3110
20	607	0.9990	594	2.3657
concentrated	597	0.9998	596	2.9000

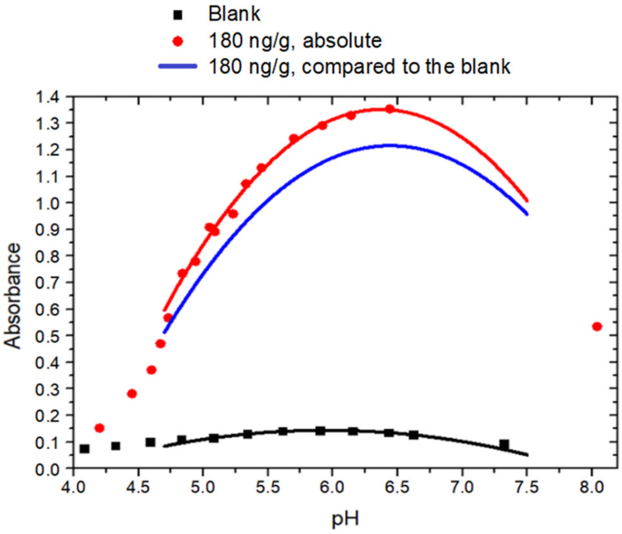

Fig. 5 The effect of pH on the measured absorbance signal

3.4 Effect of time on analytical signal

We examined how the absorbance changes as a function of time elapsed from mixing the sample and the assay solutions. This study was justified by our experience with the degradation of the common ECR-CTAB assay solution and by the fact that the color of the Al-ECR complex changes over time according to a study by Shull and Guthan [53] (these researchers did not use a surfactant, only the color of the Al-ECR complex was examined). The results are shown in Fig. 6.

It can be seen that for both the blank and the samples, it takes about 15 min for the maximum analytical signal to become detectable. This is the time required to establish a sufficient balance between the species and complexes present. However, 1.5–2 hours after the mixing, the signal slowly begins to decrease, which may be related to the ECR-CTAB degradation already mentioned in Section 2.5. Based on this, the absorbance detection must be performed within a time window of 15 to 90 minutes after the addition of the reagents. By the end of an 8-hour working day, the signal was reduced by 4.3–4.4%. This decrease for

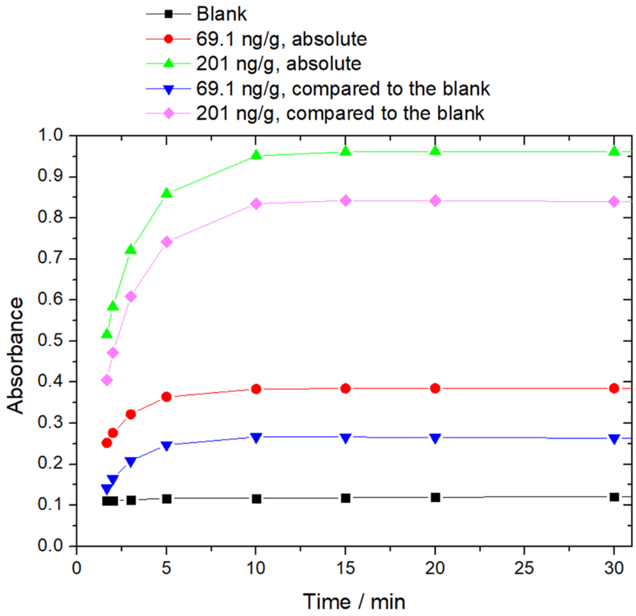

Fig. 6 The effect of the elapsed time between the material mixing and the absorbance detection on the analytical signal

the next day (24 hours after the mixing) was 27.2–28.5%. Accordingly, the relative signal loss does not depend significantly on the aluminum concentration.

3.5 Effect of temperature on analytical signal

It was also investigated the temperature effect on the change in the signal. The pH could only change slightly due to the temperature dependence of the ionic product of water. The time elapsed between the material mixing and the detection of absorbance was between 15 and 90 min for each measurement, so the time effect was eliminated. The results are shown in Fig. 7.

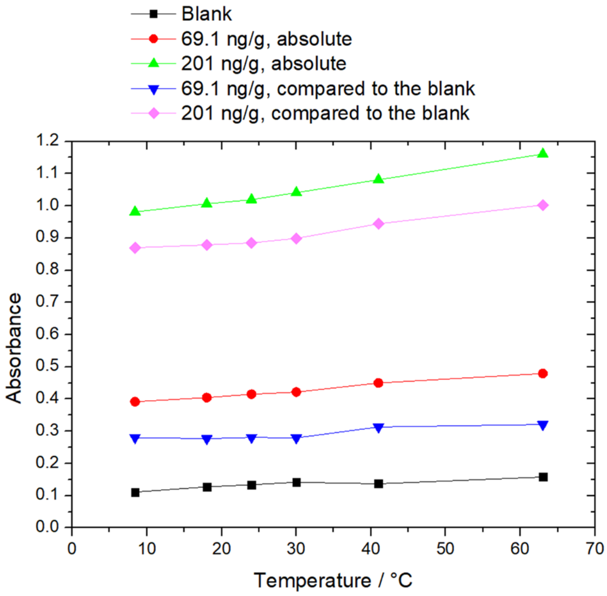

Fig. 7 The effect of the temperature on the measured absorbance signal

The temperature dependence of the signal is small, the difference of a few °C between the calibration and the measurement temperature does not cause a significant error. For samples which are significantly colder or warmer than the calibration temperature, a prior temperature adjustment is required. The change in temperature may affect the detected signal because it alters the equilibrium constants of the reactions between the Al-ECR complexes, the free ligands, the Al^{3+} ions and other Al-complexes, thereby altering the species distribution. In addition, temperature can also have an indirect effect through pH and density.

3.6 Effect of dosing sequence

Since, according to a previous study by Ferreira et al. [40], the sequence of mixing the sample, the buffer and the reagent ligand HNB (hydroxynaphthol blue ligand) has an effect on the signal, we also experimented the possibility of this phenomenon with our developed method. In our experience, there is no significant effect of the dosing sequence in the present method, and the signals detected in the different dosing sequences altered by only less than 1%.

3.7 Examination of possible interference effects

In addition to NaCl and trace amounts of aluminum, mined rock salt and sea salt often contain the following contaminants: Ca, Mg, Fe, Ba, Sr, as well as SO_4^{2-} and SiO_3^{2-}. Therefore, we examined the possible interference effects of these substances, however, we did not experience any significant effect in the amount shown in Table 2, which quantities roughly correspond to (or are higher than) the contaminant content generally present in mined rock salt and sea salt. In no case did we find a difference of more than 5% between the results of our and ICP-OES method, in the case of samples with an aluminum content of 200 ng/g. Based on this, our developed method can be advantageously used to determine the aluminum content of brine solutions used in the chlor-alkali industry.

Table 2 Examination of possible interference effect. No interference effect was observed in 25 w% rock salt solutions containing the indicated amount of pollutants.

Contaminant	Non-interfering content
Ca	1000 mg/kg
Mg	20 mg/kg
Fe	10 mg/kg
Ba	0.1 mg/kg
Sr	5 mg/kg
Na_2SO_4	15 g/l
Si	20 mg/kg

3.8 Analytical performance characteristics and validation of the measurement method

Our developed method was validated by re-measuring standard solutions with known concentrations and by comparing measured concentrations of real industrial samples with the ICP-OES method. The industrial samples were obtained from different sampling points of the salt-dissolving unit of the chlorine plant operating at the site of BorsodChem Ltd. in Kazincbarcika (Hungary). At this plant, which is part of the Chinese-owned Wanhua Chemical Group, chlorine production is carried out by membrane cell electrolysis of rock salt. The results obtained are shown in Table 3.

Our method works satisfactorily, for both the back measured and the compare measured samples most of the results were within 5% of the agreement with the actual standard concentration and the concentration measured with the ICP-OES method, deviations of more than 10% were observed only below 10 ng/g.

The analytical performance characteristics of the developed method and the molar absorption coefficient are summarized in Table 4. The detection limit was the concentration corresponding to 3 times the standard deviation of the blank's signal, and the quantification limit was the concentration corresponding to the 10-fold standard deviation of the blank's signal. The data given (except the molar absorption coefficient) refer to the original sample before dilution with reactants.

Table 3 Validation datas for our developed measurement method

Comparison with standard solutions			Comparison with ICP-OES results		
c_{ref} ng/g	c_{measured} ng/g	Recovery	c_{ref} ng/g	c_{measured} ng/g	Recovery
5.72	7.22	1.262	85.1	89.2	1.048
9.82	11.42	1.163	123	125	1.016
20.6	20.9	1.015	154	147	0.955
48.6	48.1	0.990	202	198	0.980
99.7	100.0	1.003	220	222	1.009
204	200	0.983	288	287	0.997
304	297	0.975	350	339	0.969
455	454	0.998	401	407	1.015

Table 4 Analytical performance characteristics of the method

Limit of detection	2.5 ng/g
Limit of quantification	8.4 ng/g
Sensitivity	2.897 g/µg
Molar absorption coefficient	1.05×10^5 L/(mol cm)
Linear range	8.4–690 ng/g

4 Conclusions

Based on our results, the aluminum can be determined photometrically with ECR complexing agent in the presence of cationic surfactant CTAB even in the case of nearly saturated NaCl-containing samples in the concentration range of 8.4–690 ng/g. We have also shown that increasing the salinity significantly improves the sensitivity of the method. However, assay solutions are used instead of solid reactants for ease of handling – thus the starting sample is diluted –, a similar dynamic range can be achieved as would be obtained with solid reactants for NaCl-free solutions.

It was also shown that the higher salinity increases the optimal pH of the method. In addition, it was found that due to the formation of complexation equilibria and ECR-CTAB degradation, the absorbance detection should be performed in a time window of 15–90 minutes after the addition of reactants and buffer. The optimal wavelength in concentrated saline media was 596–597 nm. The dosing sequence of the reagents, buffer, and the sample had no effect on the result, and there is no disturbing interference effect with other contaminants generally present in mined rock salt or sea salt solutions. The measurement must be carried out at the calibration temperature or at a temperature that does not differ with more than a few °C.

Since it has been found that increasing the pH to 6–6.5 increases the detectable signals and thus the sensitivity, subsequently we also design measurements in this pH range using appropriate buffer systems. However, based on our experience and knowledge to date, the measurement does not work with buffer systems commonly used in this pH range, such as phosphate, malonate, citrate buffers, which can be attributed to precipitation or complexation reactions with aluminum ions or cause other interference effects. Relatively inert biological buffers such as HEPES, MOPS, TRIS may be promising for this purpose [62].

The advantage of our method is its simplicity, speed and the fact that it does not require significant instrumentation, it can be performed with a general UV-Vis spectrophotometer, as opposed to the ICP-AES or GF-AAS methods. Another benefit of the developed method is that it is also capable of selectively measuring the aluminum content in dissolved, ionic form, compared to, for example, the ICP-OES method. An example of possible application is the examination of the ion exchange process, since the functional groups of the ion exchange resins also only react with the dissolved aluminum content. Such ion exchange resins are widely used in the chlor-alkali industry to remove aluminum and other impurities from process waters in order to protect the membrane of the electrolysis cell. The method we developed is therefore also suitable for an important task that previously represented a lack of knowledge. Our method can be used both in an industrial environment and in investigations for scientific purposes.

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