

An Improved Liquid Chromatographic Method for Determination of Aluminium in Sodium and Potassium Chloride Brine using Spectrophotometric Detection

Uvaraj M*, Surendiran A

Metrohm India Private Limited, Chennai, Tamil Nadu, India

ABSTRACT

The quality of feed brine solution required for a modern chlor-alkali plant equipped with membrane cell is much more stringent. The electrical efficiency of the membrane is easily compromised by the presence of various anionic and cationic impurities [1]. Aluminium is one the impurity which will form aluminosilicate precipitate when reacts with silicate. This will affect the membrane performance and sometimes even damages the membrane. Hence monitoring and controlling aluminium concentration is very crucial. There are many techniques and methods available for aluminium determination [2-5]. However many techniques fails to quantify aluminium concentration in trace level, especially in brine sample matrix. Chelation chromatography is one of the liquid chromatography techniques which can be used to quantify Aluminium in trace level using spectrophotometric detection [6-8]. The proposed method can be used to quantify trace level of aluminium in brine sample matrix. Aluminium forms complex with 8-hydroxy quinoline and detected using spectrophotometric detection method. This method does not require any derivatization.

Keywords: Chelation chromatography; Aluminium content; Brine solution; UV-Visible detection; Reversed phase column

Abbreviations: Ion Chromatography (IC); Atomic Absorption Spectroscopy (AAS); Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES); Gas Chromatography (GC); Limit of Detection (LOD); Limit of Quantification (LOQ); Parts Per Million (PPM); Parts Per Billion (PPB); Ultraviolet (UV); Aluminum (Al)

INTRODUCTION

The quality of feed brine solution depends on concentration of various anionic and cationic impurities [1]. A concentration of greater than 100 ppb aluminium and greater than 10 ppm silicate leads to formation of aluminosilicate complex which can damage the membrane. In order to achieve a high purity feed brine using solar salt or rock salt as a raw materials, both primary and secondary brine treatment processes are employed. During the primary treatment operation, caustic and soda ash are added together or in series to a treatment tank to initiate primary precipitation of calcium as calcium carbonate and magnesium as magnesium hydroxide. This is followed by secondary precipitation or co precipitation of other cationic impurities such as aluminium, iron and other transition metals which are also commonly found in the feedstock salt. The secondary co-precipitation process involves physical occlusion and/or adsorption onto primary precipitates. The subsequent clarified solution is filtered through

conventional press or lead filters. Resulting filtered solution contains less than 10 ppm of calcium and magnesium. It is then introduced into a secondary treatment system equipped with cations exchange resins. All the major cations are reduced to the trace level of 50 ppb, a standing maximum concentration which membrane manufacturers accept for use in chlor-alkali membrane electrolysis. However the cationic exchange activities of most of these impurities are effective only under alkaline conditions. Thus the primary and secondary treatments are effective in removing most major cationic impurities under alkaline conditions, except aluminium and silica. At this alkaline pH, both exist in anionic form. A number of different processes have been used to remove and control aluminium concentration in alkali brine solution. One of the methods is to acidify brine solution to the pH of 2.0 to 3.0 to convert the aluminum species to the soluble cationic form Al^{3+} . It is then passed through cation exchange resin to remove aluminum. Since the brine solution is in acidic pH, hydrogen ion competes with aluminium ion for the ion exchange site. This leads

Correspondence to: Uvaraj M, Metrohm India Private Limited, Chennai, Tamil Nadu, India, Tel: + 919940047837; E-mail: chemuva@gmail.com

Received: March 03, 2021; **Accepted:** March 17, 2021; **Published:** March 24, 2021

Citation: Uvaraj M, Surendiran A (2021) An Improved Liquid Chromatographic Method for Determination of Aluminium in Sodium and Potassium Chloride Brine using Spectrophotometric Detection. J Chromatogr Sep Tech 12: 442

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to lesser efficiency. Likewise there are many different methods are available to remove aluminum from brine solution. Finally aluminum concentration has to be quantified to ensure that, it is within the specified limit. There are many methods available to quantify aluminum [2,3,9,10]. One of the classical methods is by spectrophotometry using coloring agents [5]. However trace level quantification especially in brine matrix is very difficult. Atomic absorption spectrometry also can be used for aluminum quantification. But again sensitivity is very less. Sample matrix also creates lot of problems. There are many chromatographic methods available for aluminum quantification [2,6,7,9,11,12]. After derivatization, aluminum can also be analyzed by Gas chromatography [4]. But repeatability and reproducibility completely depends on derivatization. This method is also not suitable for complex brine matrix. Ion exchange chromatography method is also available for aluminum quantification [2,9,13]. It works well for simple sample matrix like water. However brine sample contains very high concentration of alkali metals. This affects the ion exchange separation of aluminium. So ion exchange method is not suitable for brine sample matrix.

The proposed chelation chromatographic method is a simple and straight forward technique suitable for brine sample matrix. It is a type of column chromatography in which ions in solution can be complexed and separated as chelation complex on a reversed phase column [6,7,14]. Chelating reagent (which is having opposite charge) forms a stable complex with analyte ion and thereby reduces charge and increases hydrophobicity. It is then separated using reversed phase column. There is no derivatization and complicated sample preparation is involved in this method. In this method, aluminium forms stable chelation complex with 8-hydroxy quinoline. The complex is then separated using reverse phase column and detected by spectrophotometric detection method [15]. This method is well suitable for alkali brine solution analysis. Alkali metals ions will not form a complex and thereby don't interfere during the analysis. Spectrophotometric detection method is very selective and many of the sample constituents don't interfere with this detection method. Reverse phase column with mixture of 8-hydroxy quinoline, acetonitrile and sodium acetate eluent is used for the separation. It is then detected using UV-Visible detector at wavelength of 390 nm. The proposed chelation chromatography method is suitable for trace level analysis of aluminium in brine sample matrix.

MATERIALS AND METHODS

Apparatus

A 930 Compact IC flex Ion Chromatography instrument from Metrohm (Herisau, Switzerland), together with 858 Professional IC Sample Processor was used. 944 Professional UV-Visible Diode Array detectors with wavelength range 190 nm–900 nm. These instruments were controlled and data acquisition was done through the MagIC Net 3.0 software. High pressure dual piston pump was used to deliver eluent at the flow rate of 1 mL/min. Prontosil 120-5-C18 AQ medium capacity reverse phased column

was used for the separation (Figure 1)

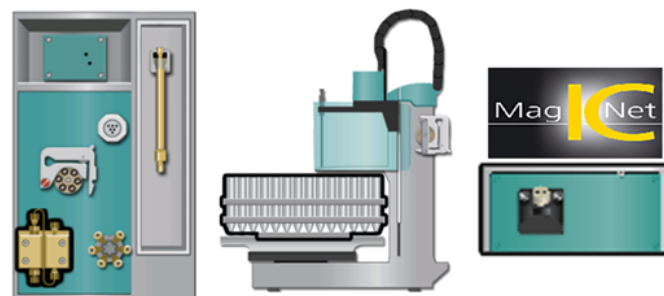


Figure 1: Instrument setup.

Chemicals and reagents

All solutions were prepared using ultrapure water (>18 MΩ) purified by an Elga Purelab Flex 1 system (Elga Veolia, UK). Sodium acetate (Merck emparta), Acetonitrile (HPLC grade), Aluminium nitrate nonahydrate (Sigma Aldrich) and 8-hydroxy quinoline (Sigma Aldrich) (Figure 2)

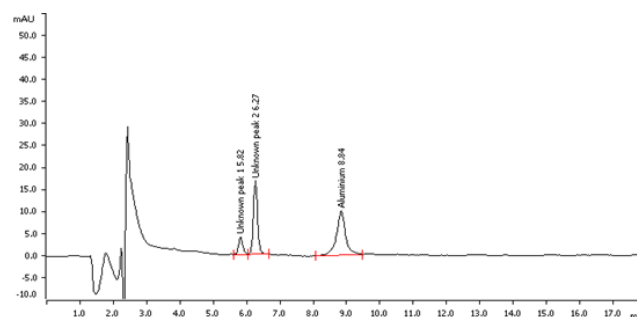


Figure 2: Column: Prontosil 120-5-C18 column.

Eluent preparation: Solution-1: 20 mmol/L sodium acetate, pH adjusted to 5.9 with acetic acid

Solution-2: 100% Acetonitrile

Eluent: 5 mmol/L 8-hydroxy quinoline is prepared in 3:2 mixtures of solution 1 and solution 2. Al (III) standard stock solution of 1000 ppm was prepared from the aluminium nitrate nona hydrate salt by diluting with eluent. All the lower level standards are prepared by diluting the stock solution with eluent.

Sample preparation

Around 1 g of sample is weighed accurately and transferred into a clean 10 mL volumetric flask and diluted upto the mark with eluent. It is then filtered through 0.2 µm filter paper and then injected into the ion chromatograph system.

RESULTS

Method specificity

Blank solution and Standard solution were injected to check the specificity. In blank solution analysis, no peak was observed at the

retention time of aluminum. This shows that method is specific.

Linearity

Al (III) standard concentrations of 5, 10, 25, 50 and 100 ppb were prepared by diluting 1 ppm stock Al (III) standard with eluent. The prepared low-level concentrations were injected to check the linearity.

A regression line was obtained by plotting peak area (mAU) of the Al (III) using the least square method. The relationship between peak response and concentration was found to be linear between the ranges of 5 to 100 ppb of Al (III), with the coefficient of determination (r²) of 0.9999 the overlay of the standard chromatograms is shown in Figure 3.

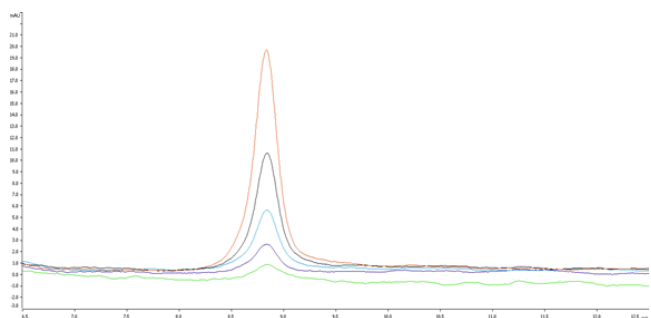


Figure 3: Overlay of aluminium standards injected for linearity 5 to 100 ppb.

Limits of detection and quantification

Based on the linearity of calibrations and the response of the Al (III) ion for the given chromatographic conditions the limit of detection (LOD) is calculated as 3 ppb and the limit of quantification (LOQ) is calculated as 10 ppb. LOD and LOQ is calculated based on signal-to-noise ratio, three times the signal-to-noise (S/N) ratio is taken as LOD and 10 times the signal-to-noise ratio is taken as LOQ.

Sample preparation

1 g of brine solution (sodium chloride and potassium chloride) is weighed accurately and transferred into a clean 10 mL volumetric flask. It is then diluted up to the mark with eluent.

Method accuracy

Method accuracy was checked by spiking study. Known amount of aluminium standard is spiked with sample and recovery value is calculated. 5 ppb of Al (III) standard is spiked with sodium chloride brine solution and spiking study was carried out (Figures 4-6). The recovery value was 103%. This shows that method is accurate. (Tables 1 and 2)

Table 1: 5.0 ppb aluminium standard repeatability data

Standard injection	Area (mAu) * min
Injection 1	0.433
Injection 2	0.459
Injection 3	0.441
Injection 4	0.409

Injection 5	0.441
Injection 6	0.448
Mean	0.439
RSD	3.80%

Table 2: 50.0 ppb aluminium standard repeatability data

Standard injection	Area (mAu) * min
Injection 1	3.303
Injection 2	3.369
Injection 3	3.324
Injection 4	3.307
Injection 5	3.346
Injection 6	3.308
Mean	3.326
RSD	0.80%

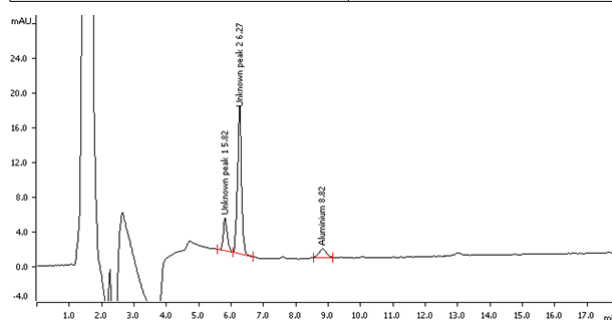


Figure 4: Sodium chloride brine solution. Result: Aluminium content - 26.4 ppb

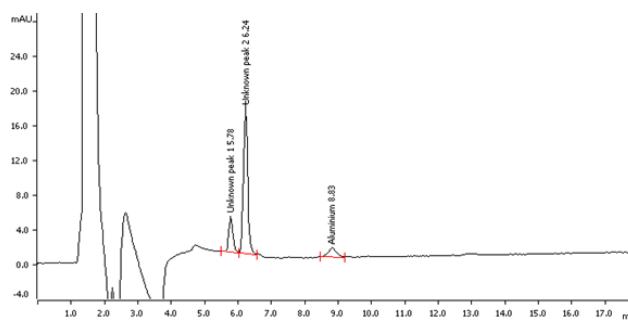


Figure 5: Potassium chloride brine solution. Result: Aluminium content - 32.3 ppb

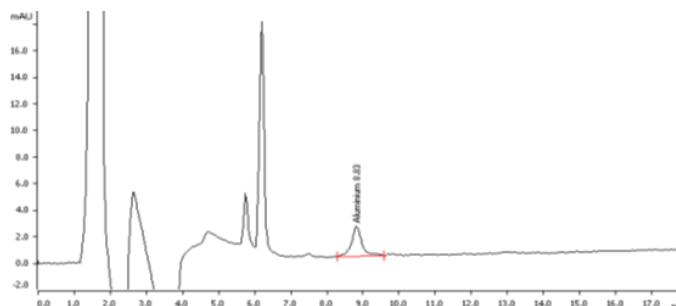


Figure 6: Sodium chloride brine solution spiked with 5 ppb aluminium standard. Result: Spiking recovery: 103 %

Repeatability

5 and 50 ppb aluminium standards were injected six times. RSD found to be less than 5% (Figures 7-10)

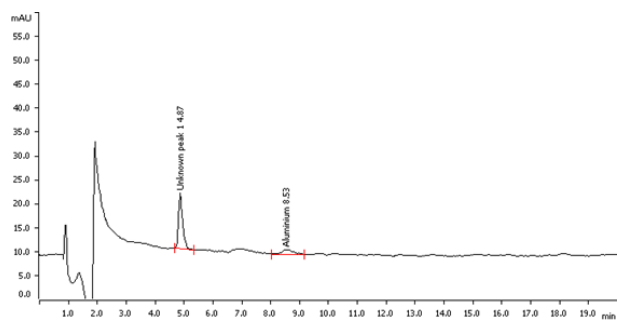


Figure 7: 5 ppb aluminium standard.

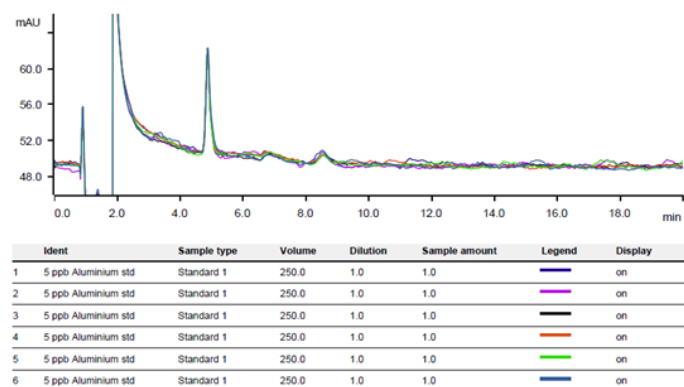


Figure 8: Overlay for six replicated injections of 5 ppb aluminium standard.

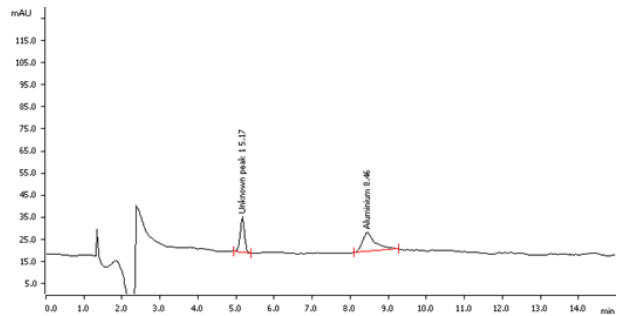


Figure 9: 50 ppb aluminium standard.

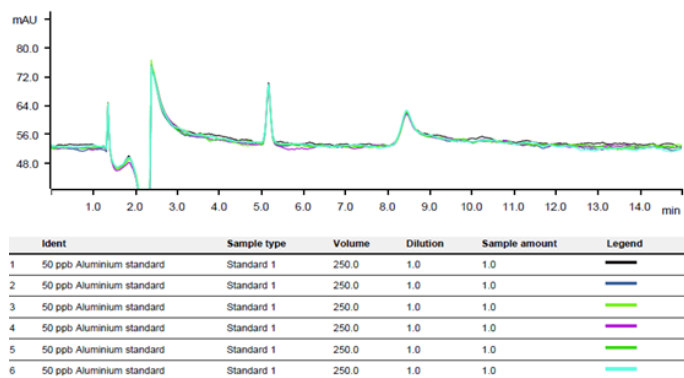


Figure 10: Overlay for six replicated injections of 50 ppb aluminium standard.

Effect of wavelength change

50 ppb aluminium standard was analyzed at three different

wavelengths viz. 380, 390 and 400 nm. Sensitivity was more at 380 nm. However it was closer to solvent cut off. Hence 390 nm was selected for the analysis (Figures 11-15)

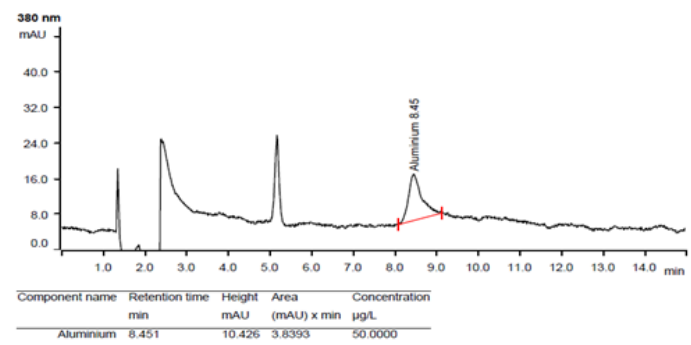


Figure 11: 50 ppb Aluminium standard analyzed at 380 nm wavelengths.

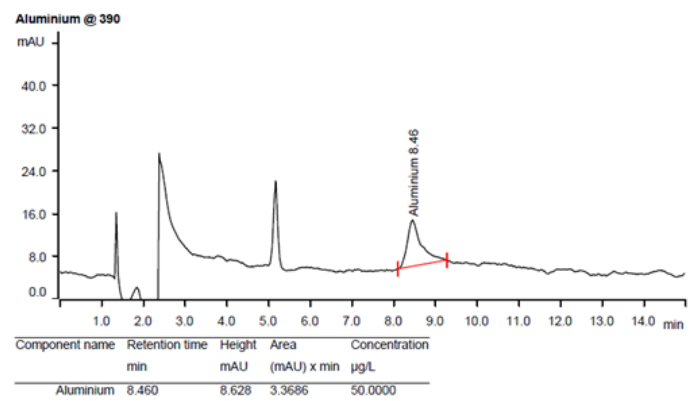


Figure 12: 50 ppb Aluminium standard analyzed at 390 nm wavelength.

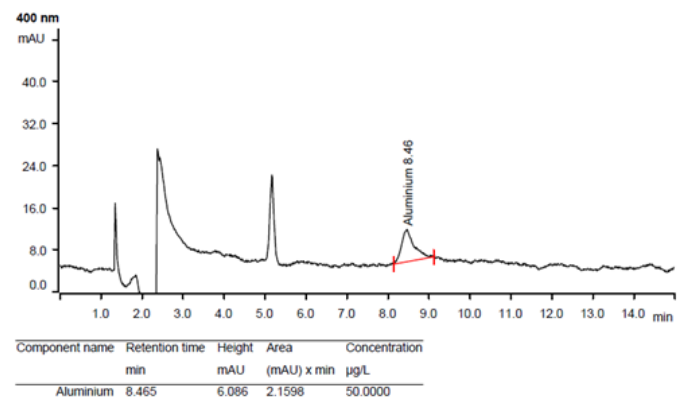


Figure 13: 50 ppb Aluminium standard analyzed at 400 nm wavelength.

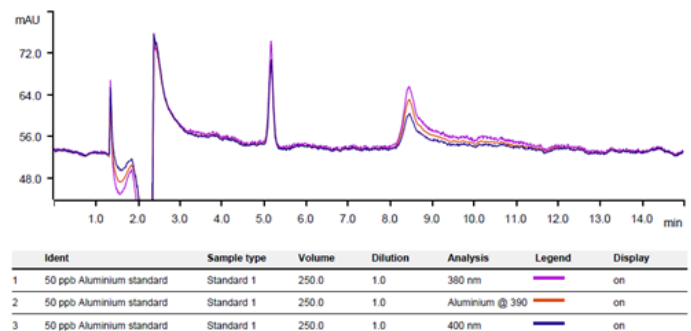


Figure 14: Overlay of 50 ppb Aluminium standard analyzed at three different wavelengths 380, 390 and 400 nm.

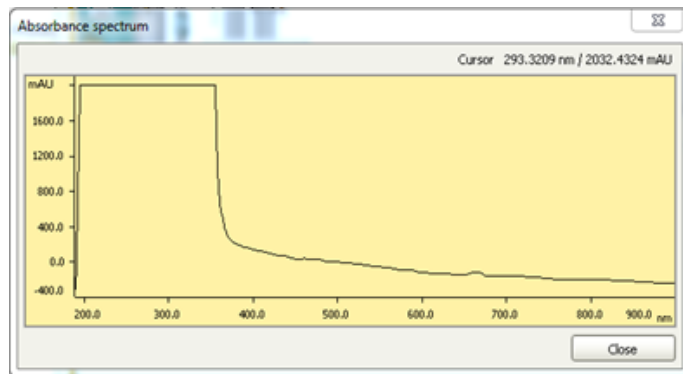


Figure 15: Eluent absorbance spectrum (380 nm near to the eluent absorbance).

Effect of acetonitrile concentration

50 ppb aluminium standard was analyzed with eluent having 5% lower and higher concentration of acetonitrile (compare to actual concentration of acetonitrile in the eluent). Retention time was decreasing with increasing acetonitrile concentration (Figures 16 and 17) (Table 3). Hence acetonitrile addition has to be accurate to get stable retention time. Even small change in retention time will not affect the result as new calibration is performed with every fresh eluent; retention time is also updated.

Table 3: Effect of acetonitrile concentration on retention time

Acetonitrile concentration (%)	Retention time (min)
35	9.7
40	8.5
45	6.5

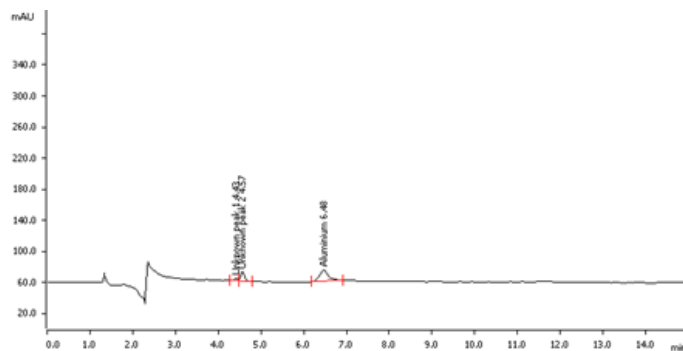


Figure 16: Effect of acetonitrile in the eluent (5 mmol/L 8-hydroxy quinoline is prepared in 2.75:2.25 mixer of solution 1 and solution 2 (45% acetonitrile)

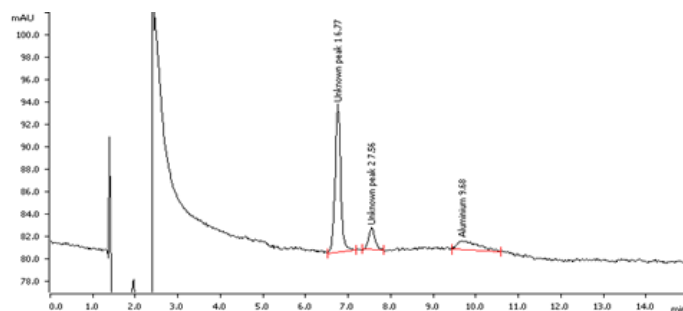


Figure 17: Effect of acetonitrile in the eluent (5 mmol/L 8-hydroxy quinoline is prepared in 3.25:1.75 mixer of solution 1 and solution 2 (35% acetonitrile)

mmol/L 8-hydroxy quinoline is prepared in 3.25:1.75 mixer of solution 1 and solution 2 (35% acetonitrile)

Effect of pH

50 ppb aluminium standard was analyzed with different pH viz 5.5, 5.9 and 7.0. Retention time was seems to be almost same. However peak shape was going bad when pH was decreased to 5.5 (Figures 18 and 19). pH of 5.9 seems to be more suitable in all respects.

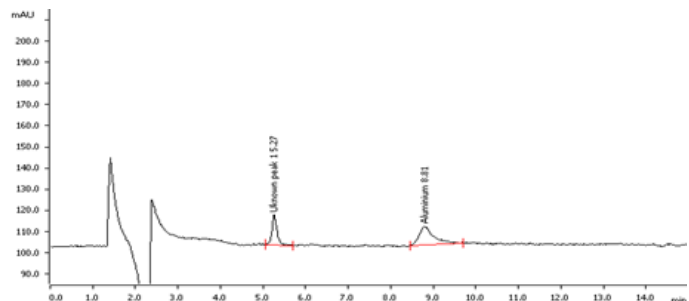


Figure 18: Effect of pH (5 mmol/L 8-hydroxy quinoline is prepared in 3:2 mixer of solution 1 and solution 2 (40% acetonitrile)

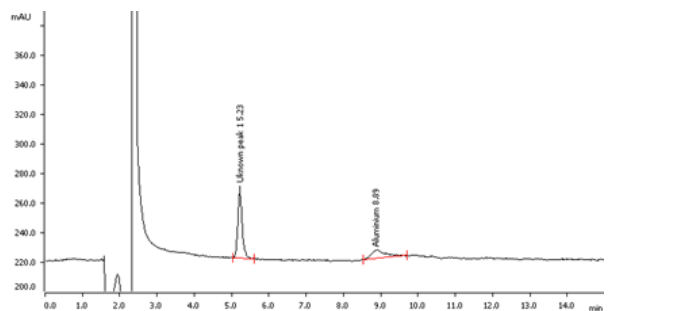


Figure 19: Effect of pH (5 mmol/L 8-hydroxy quinoline is prepared in 3:2 mixer of solution 1 and solution 2 (40% acetonitrile)

Effect of 8-hydroxy quinoline concentration

50 ppb aluminium standard was analyzed with 1 mmol/L lower and higher concentration of complexing agent (compare to actual concentration of complexing agent in the eluent). There was no much influence on retention time. So even small variation in the concentration of complexing agent will not have any influence in the final result.

Interferences study

Different possible interfering metal standards were injected. Separation was found be good with given eluent composition. Brine sample may have calcium and magnesium impurities. Hence these standards were also injected to check the interference. From the data it is clear that, presence of other metals will not have any influence on aluminium result (Figures 20-24)

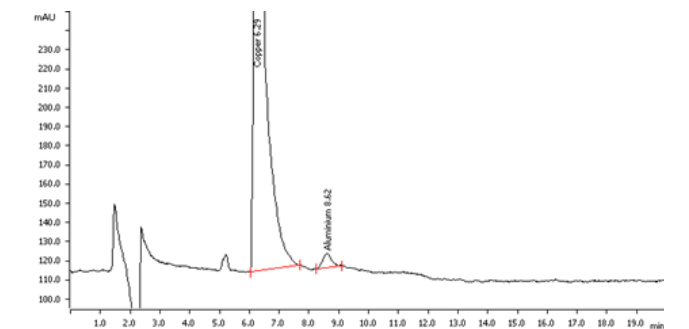


Figure 20: Interference study: Aluminium in presence of copper.

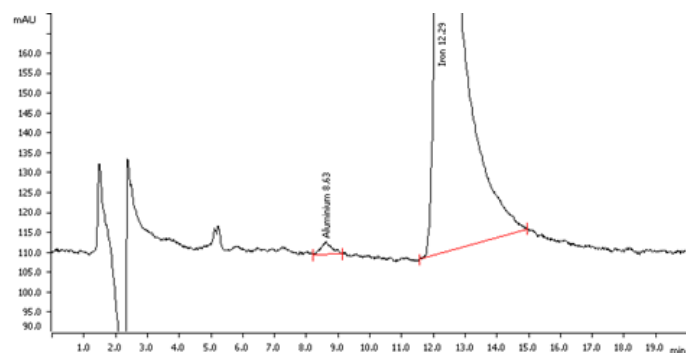


Figure 21: Interference study: Aluminium in presence of iron.

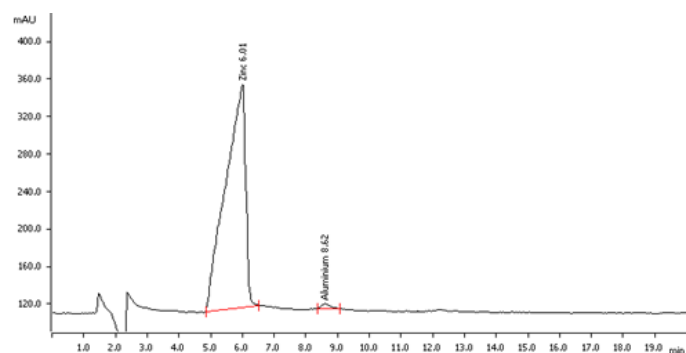


Figure 22: Interference study: Aluminium in presence of zinc.

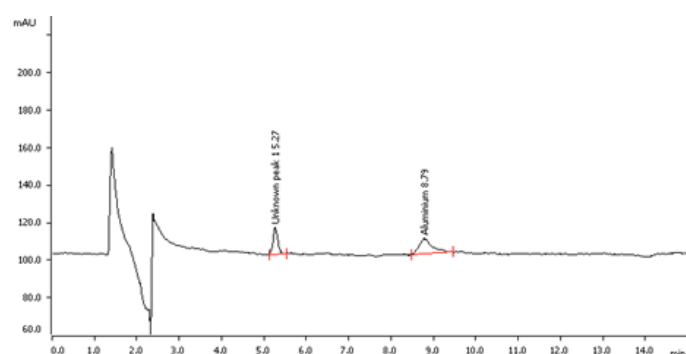


Figure 23: Interference study: Aluminium in presence of calcium and magnesium.

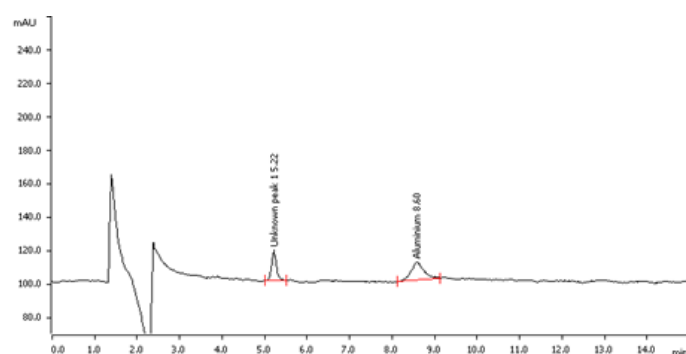


Figure 24: Effect of complexing agent concentration in eluent (6.0 mmol/L 8-hydroxy quinoline)

DISCUSSION

There are many ion exchange methods are available for aluminium analysis [2,9]. Those are based on separation using cation exchange column. Aluminium has strong interaction with cation exchanger. Those methods have many limitations in terms of repeatability, sensitivity etc. Also these methods are not suitable for real sample matrixes. Especially sample matrixes like

sea water, brine solutions can't be handled with those methods.

Few other techniques like spectrophotometry, atomic absorption spectroscopy, voltammetry are available for aluminium analysis [5]. However every method has some limitation intemrs of sensitivity, repeatability and sample matrix effects.

The proposed chromatographic method for the quantification of trace level Aluminium using chelation chromatographic method with UV-Visible detection is well suitable for brine sample solution analysis. The limit of detection for aluminium (III) is well within the minimum expected level as per brine solution specification. Sample matrix does not affect the method accuracy. The proposed method satisfies all the requirements for the determination of trace level aluminium in sodium and potassium chloride brine solution. This method does not require any derivatization. Sample can be analyzed directly after simple dilution. Detection method is also very selective and specific. Sample other constituents will not affect the aluminum result. Method accuracy is also confirmed by spiking study. Total analysis time is also only 15 minutes.

CONCLUSION

A simple and rapid method has been optimized for the determination of trace level aluminium in brine solution by chelation chromatography with spectrophotometric detection method. Reversed phase C18 column was used for the separation. This method is well suitable for brine solution which is having highly concentrated alkali metals. There is no special sample preparation or derivatization required prior to analysis. This method has lot of advantages compared to other methods like spectrophotometry, AAS, Ion exchange chromatography, Gas chromatography etc. This method can be used for any alkali brine solution like sodium chloride, potassium chloride. UV-Visible detection method is used at 390 nm wavelength. Detection limit is also well within the expected specification range of brine solution.

ACKNOWLEDGEMENTS

This work was supported by Metrohm India Private Limited and we greatly acknowledge their support.

REFERENCES

1. Biplop KP, Li shu, Veeriah J. A review on the management and treatment of brine solutions. *Environmental science*. 2017; 3(4).
2. Nancy E. Fortier, James S. Fritz separation and determination of aluminium by single- column ion chromatography. *Talanta*. 1985; 32(11).
3. Marcin F, Anetta Z. Speciation analysis of aluminium and aluminium fluoride complexes by HPLC-UVVis. *Talanta*. 2010; 82(5): 1763-9.
4. Moshier RW, Schwarberg JE. Determination of iron, copper and aluminium by gas-chromatography. *Talanta*. 1966; 13(3):445-56.
5. Ahmed MJ, Hossan J. Spectrophotometric determination of aluminium by morin. *Talanta*. 1995; 42: 1135 -1142.
6. Phil J, Pavel NN. High-performance chelation ion

- chromatography: A new dimension in the separation and determination of trace metals. *J Chromatogr A*. 1997; 789 (1): 413-435.
7. Tria J, Haddad PR, Nesterenko PN. Determination of aluminium using high performance chelation chromatography. *J Sep Sci*. 2008; 31(12):2231-8.
 8. Jingdong P, Shaopu L, Chuanyue D. Separation and determination of aluminium (III), Vanadium (V), Iron (III), Copper (II) and Nickel (II) with CALKS and PAR by RP-HPLC. *Analytical Sciences*. 2005; 21 (3): 259-262.
 9. MA Chaudry, Noor-Ul-Islam, Z Yasin. Separation and analysis of aluminium by cation exchange chromatography. *J Rad Nucl Chem*. 1988; 122(1): 43-50.
 10. Phil Jones, Les Ebdon, Tim Williams. Determination of trace amounts of aluminium by ion chromatography with fluorescence detection. *Analyst*. 1988; 113(4): 641-4.
 11. Heena R, Rajesh K, Susheela R, Ashok KM. Development of a rapid and sensitive method for determination of aluminium by reverse phase chromatography using a Fluorescence detector. *J Chromatogr Sci*. 2014; 53(5): 800-6.
 12. Masami S, Kazuhiko K, Ai M, Kazunori S, Atsuko N. Determination of trace level aluminium in environmental and biological fluids by Reversed phase ion pair chromatography with fluorescence detection using 5-sulfoquinoline-8-ol. *Current Chromatography*. 2016; 3(2).
 13. Natasa Gros. Ion chromatography analysis of sea water brine and related samples. *Water*. 2013; 5(2): 659-676.
 14. Ryan E. Meaney M. Determination of trace level copper, aluminium and iron by reversed phase liquid chromatography using novel on line sample preconcentration technique. *Analyst*. 1992; 117(9): 1435-9.
 15. Les Ebdon, Howard W. Handley, Philip Jones, Neil W Barnett. The development of an automated HPLC system for the determination of trace metals in concentrated brine and its application to process monitoring. *Microchimica Acta*. 1991; 104: 39-47.