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Extraction of small amounts of lithium from natural brines

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Abstract: Lithium is a very strategic metal and the world's energy supply source in the future. Brines that have lithium are mainly chloride brines, which are highly variable in terms of lithium and other metal ion concentrations. The economic isolation or extraction of lithium from such sources depends not only on the amount of lithium which is present, but also depends on the concentration of interfering ions such as calcium and magnesium. If the amount of magnesium is low, isolation by sediments with lime is possible and economically justified. The possibility of using photo-evaporation is also considered as another important method. A solution containing two millimoles of salicylaldehyde and one millimole of 2 & 6-diaminopyridine in 10 ml of ethanol was percussed for one and a half hours. The reaction mixture was cooled in an ice-water bath to form a yellow precipitate. This collected sediment was washed with 5 ml of distilled water. Then it was recrystallized and purified by ethanol. The results showed that the good yielding complexity of lithium ion with the Schiff base ligand is 2, 2-pyridine 6, 2-diylys (nitrile). Also, the results show the very good efficiency of the method for extracting of lithium ion in synthetic and natural aqueous samples. For this reason, this method can be used to measure the impurity values of lithium ion in synthetic and natural samples.

Keywords: Lithium, brine, sediment, natural, concentration.

Introduction

Lithium is one of the most widely used metals in various industries, including medicine, pharmaceuticals, electronics, regulatory industries, nuclear reactor coolants, ceramics, glass, and aerospace alloys. Due to its special lightness, lithium metal is widely used in the aerospace industry, and on the other hand, it is also used more in the production of energy storage batteries. A country like Germany is lacks of lithium resources.

Lithium is one of the rare elements on earth, and in recent years, metallic lithium and its various compounds have found very important applications, especially in industry, energy and pharmaceuticals. Extraction of lithium from brines is done in some countries, especially in South America. The increasing of demand for lithium consumption has caused special attention to the correct measurement of this element in natural samples. Natural brines have small amounts of lithium ion, but despite this small amount, about 69% of the world's lithium reserves are salt lakes. Therefore, lithium is recovered as a byproduct in the process of producing other salts from natural brines. Consequently, to extend such extraction, it is important to measure low amounts of lithium in the presence of high concentrations of other ions.

Theoretical Foundations

The brines that have lithium are mainly chloride brines, which are highly variable in terms of lithium and other metal ion concentrations. The economic isolotion of lithium from such sources depends not only on the amount of lithium present, but also depends on the concentration of interfering ions such as calcium and magnesium. If the amount of magnesium is low, extraction by sediments with lime is possible and it is proper economically. The possibility of using photo-evaporation is also considered as another important method.

Common methods are used for measuring low amounts of lithium in aqueous solutions are flame spectrometry or atomic absorption spectrometry for samples whose dry residue do not exceed from 7g/L. In natural brines, the total amount of dissolved solids (TDS) is in the range of 25-350g/L, as a result the determination of low amounts of lithium in these types of samples by atomic emission and absorption spectrometry methods has many problems due to the presence of interfering ions and the high viscosity of the sample, so a sample preparation step will be required. The molar ratio of lithium to the total cations in brines is very low and around 0.0001, so it seems necessary to develop a suitable and fast method to remove these disturbances and extract lithium and then measure it.

The interference of cations of salts in ocean water has been investigated for lithium measurement by flame photometry and the results show that it is not possible to determine the amount of lithium with arbitrary accuracy. The measurement of lithium in these samples by the flame photometry method with the standard increase method has also shown that the existing problems are partially solved.

To prevent of mentioned phenomena, organic solvent and its distillation have been used in order to extract and remove the disturbances of other salts and then measure lithium. These methods are not very desirable due to their time-consuming nature and the use of toxic and dangerous solvents. In some other methods, precipitation of interfering ions with the help of other mineral compounds is used. However, in these methods, some lithium is added with chemicals, forms a precipitate and as a result, it’s removed from the sample.

Electro-dialysis with ion exchanger membranes has been used to measure the amount of lithium in brines obtained from sea water and brines obtained from the processes of salt production industries by atomic absorption spectrometry. But the disturbance caused by the various ions in the brines and bitter-solution and the problems caused by the high viscosity of the sample still exist to determine the amount of lithium.

Recently, by using crown ethers and heteropoly-acids of sodium, potassium, calcium and magnesium ions which were exist in the form of removed sediment and then the remaining lithium in the sample was measured by flame emission spectroscopy. These methods are also not ideal due to the use of expensive materials and the possibility of removing some quantity of lithium along with disturbing ions.

In order to recovering of lithium and other valuable elements from sea water and lakes, crystallization processes of step by step precipitation, ion exchange process and solvent extraction process have been used traditionally. But these processes have not been very favorable for the industry due to environmental problems, high cost, low selectivity and low concentration of lithium in brines. Compared to these traditional processes, the absorption process is a more economical and environmentally friendly process and prevents the production of harmful wastes. Absorbers with manganese oxide and aluminum were produced by Russian researchers; but they did not show good results for the selective recovery of lithium. In another study, adsorption of H_2TiO_3 showed high selectivity absorption ability for lithium in a solution containing interfering elements of alkali metals, but the absorption capacity for ion of lithium was low.

In this research, the complexation reaction of cations Ni^{2+}, Cu^{2+}, Pb^{2+}, Li^{2+}, Ca^{2+} and Nai^{2+} with the ligand 2.2-pyridine 2.6-di-ylbis in ethanol solvent at 25 degrees Celsius, was investigated by conductometric method and it was found that this ligand forms a stable complex with ion of lithium. As a result, this ligand has been used to modify the C18 disk and it use to pre-concentrate the low amounts of lithium ion that present in two natural brine samples and measure it by flame photometry.

Schiff bases with having electron donating atoms in their structure have a very good ability to complex metal ions. On the other hand, the organic nature of these compounds has caused them to be used in the studies of liquid extraction, solid phase extraction, cloud point extraction, competitive transfer of cations through the liquid membrane, preparation of ionizing electrodes and electrochemical sensors.

Applications of lithium

Due to its unique physical and chemical properties, lithium and its compounds can be divided into several groups with various industrial applications. In order to evaluation of using lithium in different fields, the annual compounded index of growth rate should be used, which is a suitable index to express the growth rate of each field in a certain period of time. Lithium as a strategic and vital metal used in many industries, the most important of which, along with the index values of the annual compound growth rate separately in each field in the 10-years period between 2003 and 2013, were as follows:

- Glass and ceramic industries (2%).
- Nuclear and military industries (lack of sufficient information).
- Lithium batteries (8.22%).
- Lubricant (3.3%).

- Air purifiers (5.2%).
- Steel industries (lack of sufficient information).
- Production of pharmaceutical and polymer products (5.2%).
- Aluminum production (4.3%).

Sources of brines

The composition of lithium in natural brines is mostly in the form of chloride, and other elements such as: magnesium, sodium and potassium are also found with it. It is necessary to pay attention to the fact that the extraction of lithium from these brines economically depends not only on the abundance of this element, but also depends on the concentration of other accompanying ions such as magnesium and calcium. Based on extensive research, researchers have come to the conclusion that Afghanistan may have 60 million tons of copper, 2.2 billion tons of iron ore, 1.4 million tons of rare soil elements such as lanthanum, cerium, and neodymium.

Experimental method (chemicals and equipment)

Chemicals: Methanol, dimethyl sulfo-oxide (DMSO) and ethanol solvents with spectroscopic grade, copper, nickel and lead nitrate salts, calcium and lithium perchlorates were used from Merck Company without purification. Schiff base ligand 2,2-pyridine 2,6-diylbis (nitrile (E) methylidene) from the reaction between salicylaldehyde and 2,6-diaminopyridine according to the reported method with 99.5% purity was synthesized and used.

Equipment: In the conductometry method, used from South of England conductivity meter equipped with a double-walled glass cell connected to the Jolabo colator (temperature setting ±0.01°C). In the solid phase extraction method, membrane disks with bonded octadecyl silica, with a diameter 47 mm, thickness 0.5 mm, particle size 8 micrometers and pore size 6 nm from Empor Company, as a solid substrate and a 47 mm standard filtering device connected to a vacuum hose, was used for the experiment and also the measurement of Atomic emission was done by using a flame photometer made by Southern England Company equipped with a lithium filter.

Work methods

A solution containing two millimoles of salicylaldehyde and one millimole of 2,6-diaminopyridine in 10 ml of ethanol was refluxed for one and half hours. The reaction mixture was cooled in an ice-water bath to form yellow sediment. This collected sediment was washed with 5 ml of distilled water. Then it was recrystallized and purified by ethanol.

First, the conductivity meter device of gradation and the constant value of the cell was determined 0.85 cm^{-1}, then 10 ml of lithium ion solution with a concentration of $5*10^{-5}$ molar in ethanol solvent was poured into the double-walled cell of the conductivity meter and after setting the temperature at 25 degrees Celsius, its conductivity was measured and recorded. Then, 10 microliters of ligand solution with a concentration of $10*5^{-3}$ molar in the same solvent was added to it by a Hamiltonian syringe, in a stepwise process, and after stirring the solution with a magnet, its conductivity was measured.

Solid phase extraction

First, in order to clean the surface of the disc from possible contamination that may exist during its manufacturing process, the disc was washed with a minimum amount of methanol. For this purpose, after preparing the extraction tools with solid phase and placing the disc in its place, first, 20 ml of methanol was poured onto the disk and allowed to pass through the disk with very gentle vacuum. After passing the methanol, 20 ml of distilled water was poured on the disc and all the methanol was allowed to pass through the disc. Then, by passing air through the disc for a few minutes, the surface of the disc was slightly dried. In all these steps, care was taken to ensure that the surface of the disc does not dry completely. In the next step, in order to modify the disk, 1 ml of dimethyl sulfo-oxide along with 1 ml of ethanol containing 5 mg of ligand was poured on the disc and via vacuum was passed through the disc. The filtrate collected solution in a test tube was again passed through the disc; this was repeated until the filtrate solution was colorless. After this step, the disc was modified by the ligand and ready for testing. Here too, the surface of the disk and the implanted ligand should not be completely dry and brittle, because in this case the extraction efficiency will be low. To perform the extraction, 100 ml of aqueous solution containing 0.005 mg ion of lithium buffered by the desired buffer was passed through the modified disk. After the complete passage of the solution, the disc was washed by 5 ml of acid solution. Then both solutions were collected and the amount of lithium in them was measured by a flame photometer.

Findings

Table1: Results related to the type and concentration of detergent phase in extraction of lithium ion.

Detergent Solution	Concentration (Molar)	Recovery percentage (%)
Perchloric acid	0.3	99.2
Perchloric acid	0.5	48.6

Perchloric acid	1.0	50.5
Nitric acid	0.7	75.2
Nitric acid	0.5	80.8
Nitric acid	0.3	84.5
Nitric acid	0.1	35.6

Table 2: Results related to extraction of lithium ion from binary mixture.

Added Cation	Concentration (ppm)	Recovering of lithium (%)
PB^{2+}	100	84
K^{+}	100	92
Ca^{2+}	100	98
Cu^{2+}	100	96
Ni^{2+}	100	92

Table3: Checking the effectiveness of method that used for measuring the amount of lithium in two samples of natural brine.

Brine Sample	Amount of added Lithium	Measured Amount of Lithium	Recovering of Lithium (%)
First brine sample	0	1.4	0.0
	10	11.3	98
	20	21.5	102.2
Second brine sample	0	1.10	0.0
	10	10.9	99
	20	21.2	102

Conclusion

The results of this research showed that the good yielding complex of lithium ion with the Schiff base ligand is 2,2-pyridine 6,2-diylis (nitrile). Also, the results showed the very good efficiency of the used method in extracting of lithium ion in synthetic and natural aqueous samples. For this reason, this method can be used to measure the impurity values of lithium ion in synthetic and natural samples.

References

Bandi K.R., Singh A.K., Upadhyay A., Electroanalytical and Naked Eye Determination of Cu2 + Ion in Various Environmental Samples Using 5-amino-1,3,4-thiadiazole-2-thiol Based Schiff Bases, Mat. Sci. Eng.: C, 34: 149-157 (2014).

Chitrakar, R., Kanoh, H., Miyai, Y., Ooi, K., "A New Type of Manganese Oxide (MnO2â0.5H2O) Derived from Li1.6Mn1.6O4 and Its Lithium Ion-Sieve Properties", Chem. Mater., 12, pp. 3151–3157, (2000).

Darezereshki, E., Ranjbar, M. and Bakhtiari, F., 2010. One-step synthesis of maghemite (γ-Fe2O3) nano-particles by wet chemical method. Journal of Alloys and Compounds, 502(1), pp.257-260.

Ecrement F., Burelli F.P., Determination of Lithium in Waters by Atomic Absorption Spectrometry, Application: use of Lithium as a Tracer in Hydrology, Analusis, 3: 146-156 (1975).

H. Park, N. Singhal, E.H. Jho., 2015; "Lithium sorption properties of HMnO in seawater and wastewater" , Water Res, 87, 320–327.

Hamzaoui A. H., M'nif A., Rokbani R., Mineral Salts Removal and Lithium Traces Determination in Highly Concentrated Solutions and Natural Brines, Talanta, 70: 847–851 (2006).

Hamzaoui A.H., A. M'nif A, Rokbani R., Contribution to the Lithium Recovery from Brine, Desalination, 158: 221-224 (2003).

Honga, H.-J., Ryua, T., Parka, I., Kimb, M., Shina, J., Kima, B.-G., Chung, K.-S., "Highly porous and surface expanded spinel hydrogen manganese oxide (HMO)/Al2O3 composite for effective lithium (Li) recovery from seawater", Chem. Eng. J., 337, pp. 455–461, (2018)

https://8am.media/afghanistans-large-lithium-ores-a-hidden-wealth-that-will-change-the-fate-of-afghanistan.

Nourifard F., Payehghadr M., Kalhor M., Nezhadali A., An Electrochemical Sensor for Determination of Ultratrace Cd, Cu and Hg in Water Samples by Modified Carbon Paste Electrode Base on a New Schiff Base Ligand, Electroanalysis, 27: 1-8 (2015).