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SAFE AND ECO-FRIENDLY DETERMINATION OF LITHIUM IN SILICATE ORES USING SINTERING AND INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY

We developed new methodologies for the quantitative determination of lithium in lithium-bearing silicate minerals and clays. This research describes direct analysis of Li in powder using an atomic-emission complex for spectrum analysis "PGS-DDP-BAES" and sintering as a sample preparation technique followed by ICP-OES analysis. A new atomic-emission complex for spectrum analysis could be used to efficiently overcome the complex matrix effects, and thus allows for the direct quantitative determination of lithium in solid samples (ores, clays). The relative standard deviation is up to 7.0%. For the extraction of Li from silicate ores and clays by sintering various parameters including sintering temperature, reaction time and additives were studied. The results indicate that the optimal temperature for sintering with NH_4Cl *and* $Ca\ CO_3$ *is at around 900°C. Optimum conditions for lithium extraction were found to be 300 °C (30 min) and 900 °C (60 min), at mass ratios of an ore :* $NH_4Cl : CaCO_3$ *of 1 : 1 : 8. In these conditions a lithium extraction degree of 92% is reached. Relative standard deviations for the method with sintering and ICP-OES analysis vary in the interval from 1.7 to 2.2%.*

Keywords: *silicate ores, clays, pegmatite, lithium, sintering.*

1. Introduction

Lithium, known as white gold, is nowadays ruling the dynamics in the raw materials market all over the world [3]. According to some estimates, global Li resources of brine, pegmatite and clay are around 45 Mt [20, 5].

Nowadays, global extractable Li reserves are estimated to reach nearly 14 Mt [6]; in future decades (2030-2050) Li consumption is expected to climb to 35 Mt [21]. The European Commission is seeking to have at least 30 million electric vehicles (EV) on the roads by the end of

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this decade [13]. In April 2022, the Canadian government committed $3.8 billion in its federal budget to implement a new critical minerals strategy over eight years [2]. US President Joe Biden invoked the Defense Production Act in March to help companies access government funding for feasibility studies for new projects that extract lithium, nickel and other EV metals [2]. The government's goal is for half of US passenger car and light-truck sales to be zero emission by 2030. For that to become a reality mining is required. Therefore, lithium will play a key part of the global EV supply chain. Furthermore, 78,600 businesses linked to new energy vehicles penetrated the industry in 2020 [27].

In 2021, batteries were by far the largest end-usage of lithium accounting for roughly 74 percent of the lithium consumption. The use of lithium in ceramics and glass made up another 14 percent [15].

Lithium is a unique element; it has the strongest charge mobility among alkali metals and the highest electrical storage density of known elements [16]. The increasing battery demand will continue to be a strong driver of lithium consumption as lithium-ion battery technology is used extensively in the production of electric vehicles [15]. There is a strong need for developing additional lithium resources to be able to meet the growing demand. The majority of today's commercial lithium production is based on lithium-rich brine reservoirs (salars) and minerals. For instance, lithium silicate minerals such as spodumene, lepidolite, and petalite are gaining importance in providing the vast quantities of raw materials required for the energy transition over the last few years [31].

The different techniques capable of extracting lithium from waste was examined by Y. Kim et al. [12]. Chemical analyses of the ore samples were undertaken using a combination of standard mixed acid digest — peroxide fusion techniques and ICP-MS or ICP-OES spectrometry [1]. The recovery of Li from spodumene reached 90%. Roasting of β-spodumene with NaF to produce LiF with a lithium extraction degree of 90%, approximately is reached by Gustavo D. Rosales et al. [24]. In addition, L. Gao et al. [7] studied recovery and leaching kinetics of lithium from lepidolite by sulfuric acid, where the Li yield could reach 97%. Nevertheless, height temperature 433 K for 4 h and sulfuric acid concentration of 60 wt.% make this method rather complicated. A four-acid assay digestion, a combination of HNO_3, HF, $HClO_4$ and HCl, is effective for almost all lithium minerals, and targeted cations in solutions can be measured using ICP-MS or ICP-OES spectrometry. If other elements such as Sn, Ta and Nb are required, a fusion digestion is recommended to ensure complete dissolution of refractory minerals which may host these elements. However, sample preparation with a four-acid assay digestion takes 2 days and the method is not adequate if a fast analysis is required [11].

The studies [26, 25] have shown that 90% Li could be extracted from β-spodumene by leaching with 7% HF at 75 °C for 20 min. The extraction of Li is highly dependent on the temperature and time. Applying a mixture of different acids (at ratios of an ore/HF/H_2SO_4 of 1 : 3 : 2 (g/mL/mL) tends to increase the recovery of lithium from natural spodumene up to 96% and helps to overcome the drawback of high energy consumption — avoiding heating during extraction process [9].

Calcination is one of the common processing techniques used throughout the extraction of lithium from spodumene. The first continuous plant to convert spodumene concentrate to lithium carbonate by calcination, roasting of calcine with H_2SO_4 and water leaching was launched in 2012 by Galaxy Resources in China [18].

Various additives (CaO and NaOH) were employed to enhance the extraction process of lithium from β-spodumene. Lithium was leached with Na_2SO_4 [14]. The lithium extraction efficiencies were recorded to be 93.30% with CaO addition and 90.70% with NaOH addition respectively.

NaOH was proposed for direct leaching of lithium from spodumene [23]. All the abovementioned methods are more environmentally friendly and economically feasible comparing to the currently industrialized sulfuric acid method. However, they demand further purification and rumination on safety relating to chemical consumption.

Methods based on inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-

MS), atomic absorption spectrometry (AAS), laser ablation ICP-MS and laser induced breakdown spectroscopy (LIBS) provide the foundation for quantitative analysis of lithium in geological samples [1]. Quantitative measurements are facilitated by analyzing well-known reference materials.

Measuring the lithium concentration in different silicate ores and silicate minerals is critical for evaluating the economical viability of industrial lithium extraction projects [4, 5, 30]. Routine analysis of lithium remains an area of active development. This requires a fast and precise approach to liberate lithium from a silicate matrix and make it detectable with standard analytical instruments. It is well-known that HF and H_2SO_4 are usually used for the digestion of silicate ores and silicate minerals [8, 10, 17, 22]. Some minerals, namely spodumene, could be digested in acids only at hard microwave radiation [29]. Furthermore, such acids are not eco-friendly and might cause serious injuries if not handled properly.

The Metso Outotec process concept is based on a two-stage alkaline leach process [19]. Silicate mineral is first destructed in a pressure leaching stage using soda ash. Lithium carbonate and analcime are the main components of the first-step reaction. In the second-step reaction lithium carbonate is converted to lithium hydroxide using $Ca(OH)_2$. The extraction yield of lithium from concentrate exceeds 90%. The Metso Outotec process concept is acid and sulphate-free as well as simple.

Therefore, the main goal of our research was to establish a simple, precise, safe, and eco-friendly method of liberating lithium in silicate minerals for the subsequent analysis of lithium concentration in ores for the industrial production of lithium compounds.

The most attractive method for extraction of Li from silicate ores and clays is the Smith method based on sintering [28]. Since this method includes the formation of alkaline chlorides, the volatility of LiCl most be considered. Therefore, we developed a method of sintering of lithium-bearing silicates that facilitate the recovery of lithium.

The atomic-emission complex for spectrum analysis "PGS-DDP-BAES" has been applied as a second approach of the direct analysis of Li in solid powder of ores and clays. The powder is sucked into the inlet system where it is heated in argon plasma, and then analyzed by atomic emission spectroscopy (AES). This technique provides rapid sample throughput.

2. Materials and Methods

2.1. Samples

Quality control samples consisting of lithium ores were examined. Certified NIST standard reference material SRM 183 (Lepidolite, 4.12% Li_2O, the USA); SY-2, a syenite from the Bancroft area of eastern Ontario (Li 0.1 g/kg); the rhyolite, RGM-1 (Li 0.07 g/kg), from Glass Mountain, Siskiyou County, California, were chosen because of their similarities to the matrix of investigated samples.

Six samples consisted of standard reference materials CP-OCH-1 (Russian spelling) with added Li_2CO_3 (prepared by the plant "Etalon", Li, %: 0.500; 0.850; 1.043; 1.565; 2.347; 4.695, USSR) were applied to the analysis of Li using "PGS-DDP-BAES" complex.

Ore (Iberian pegmatite, Spain) and clay (Nevada, the USA) have been used for method development and validation.

Calibration standards for ICP-OES measurements were prepared in 1% HNO_3 over different calibration ranges to match the expected concentrations in ores or clays.

2.2. Sample preparation techniques

Samples were prepared using different techniques: a sintering approach, a four-acid assay digestion (HNO_3 + HF + HCl + $HClO_4$), a sodium peroxide fusion, a direct solid analysis.

With a sintering approach, 0.5 g of sample, 0.5 g of NH_4Cl and 4.0 g of $CaCO_3$ were ground in an agate mortar and placed in a platinum crucible. The mixture was heated at 300 °C (30 min) and then at 900 °C (60 min).

With a four-acid assay method, 0.2 g of dried sample was treated with the reagent mixture (3 mL HCl, 2 mL HNO_3, 1 mL $HClO_4$, and 2 mL HF) at 110 °C. The procedure takes approximately two days and must be completed under a perchloric-acid fume hood.

With a sodium peroxide fusion, normally 0.2 g of sample was mixed with sodium peroxide in the ratio of 1 to 4 and fused for 15-30 minutes at about 800 °C. After fusion, the melt is cooled down and dissolved in water.

With a solid-sample accessory, a sample of ore or clay was directly analyzed after grinding. RSMs that contain known amount of Li were prepared in the same manner as the unknown samples of ores and clays.

2.3. Atomic-emission complex for spectrum analysis "PGS-DDP-BAES"

An atomic-emission complex for spectrum analysis was made in the Institute of Geological and Ecological Matters of Donbass by Dudik O.M. It includes a spectrograph PGS-2, a two-jet arc plasmatron DDP-50T, an accessory to introduce a liquid sample or a powder sample into plasma, a multi-channel analyzer of atomic emission spectra BAES-10 and a computer program of registering emission spectra "Spektro Wizard". Spectrum is registered using 8 photodiode lines.

This laboratory complex allows to measure quantitatively the content of chemical elements in solid samples (powders), as well as in solutions. It can simultaneously determine more than 70 elements (from lithium to uranium) with high accuracy in the range from $n \cdot 10^{-8}$ % to $n \cdot 10$ % by mass.

The physical principle of the method. The substance evaporates in the light source — plasma. Additional excitation energy is given to vapors of the substance; as a result the light emission of atoms of chemical elements occurs. The emission spectrum is unique for each chemical element and consists of spectral lines characterized by a certain wavelength.

The principle of operation of DDP-50. Electrical energy is converted into an arc discharge between the cathode and the anode (heads) of the plasmatron located at a certain angle. Discharge is supported by the fusion of two argon plasma jets blown from the cathode and the anode. Samples (powders or liquids) are introduced between the plasma jets along the axis of the main flow.

The estimation of mass fractions of chemical elements is carried out with the help of a multi-channel analyzer of atomic emission spectra BAES-10 (author V.A. Yegorov) which is located instead of photocassettes on the PGS-2 spectrograph. It combines all the positive qualities of photo plates and photoelectronic multipliers and is devoid of their disadvantages. It consists of a photo receiving unit, completed on the basis of a micro-assembly of thermally stabilized photodiode lines, in the amount of eight lines, an interface for a computer. BAES-10 has a wide range of spectral sensitivity, a wide dynamic range, high quantum sensitivity (up to 95%); it is characterized by the absence of restrictions on the number of lines, the possibility of analyzing the shape of the line, considering the background under the line. Automatic calibration of the spectrum is performed; database and archives are entered, which allows instant output of results and simultaneous multi-element analysis of geological objects of different nature and composition (ores, rocks, soils, industrial waste, liquids, etc.).

The software package "Spektro Wizard" (author S.A. Yegorov) provides the analyst with a wide range of possibilities: visualization and measurement of the intensity of spectral lines, construction of graphs, calculation of mass fractions of elements in samples, metrological evaluation and statistical processing of measurement results. Results of analyses are displayed on the screen. The software package could add spectroanalytical information into the database.

Currently, the "PGS-DDP-BAES" analytical complex is installed (relocated from Donetsk) at the Institute of geochemistry, mineralogy and ore formation named after M.P. Semenenko of the National Academy of Sciences of Ukraine.

2.4. Equipment and instrumental conditions

All analyses at the laboratory of K-UTEC were performed on a SpectroBlue (Spectro, Germany) fully simultaneous ICP-OES applying the operating parameters: plasma power 1400W, plasma gas flow 15 L/min, nebulizer gas flow 0.8 L/min, auxiliary gas flow 1.2 L/min.

All analyses at the laboratory of Karlsruhe Institute of Technology (KIT) were performed with the ICP-OES (iCAP 7000, Thermo Fisher).

Particle size distribution of ore was determined with Mastersize 300 (Malvern, the United Kingdom).

Platinum crucibles with lids were two types — a wide-form crucible (top inner diameter 34 mm, bottom inner diameter 21 mm, depth 25 mm) and a high-form crucible (top inner diameter 25 mm, bottom inner diameter 14 mm, depth 80 mm).

To assess the mineralogy of solid samples at the laboratory of KIT, the powder of Iberian

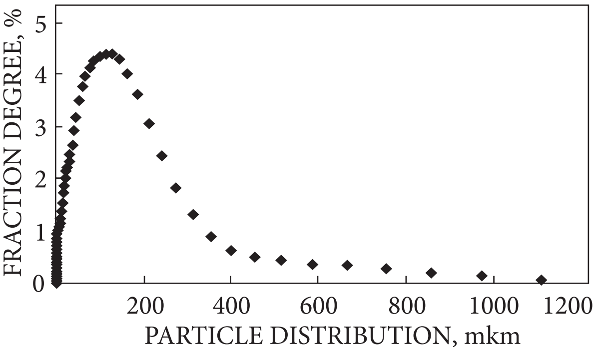

Fig. 1. Distribution of particle sizes

pegmatite was characterized by X-ray diffraction (D8Discover, Bruker). A sample was measured with a step of 0.01° (2-Theta) using the software Eva (Bruker). The peaks' position and intensity of a sample are compared with the patterns of powder diffractograms from various diffraction database references.

3. Results

To decompose silicate geological samples, acid mixtures such as HF/HNO$_3$, HF/HClO$_4$, HF/H$_2$SO$_4$, HF/HNO$_3$/HCl, and HF/HClO$_4$/HNO$_3$ have been used extensively in closed vessel digestions for multielement analysis [11]. The handling of strong acids requires time consuming procedure and a height level of safety. Therefore, we would suggest rapid digestion with shortened time as well as it requires lower safety precautions. Complete digestion of a sample is a precondition to achieve reproducible and accurate results in routine analyses.

Geological samples must be properly ground and dried before the analysis. Therefore, ore and clay samples are pulverized and ground into a fine powder. The finely ground powder is mixed to ensure homogeneity and then glass bottles are filled up with it. The Figure 1 shows particle size distributions for micro-scale ore powder. This figure makes it apparent that the distribution is unimodal and the fraction degrees of particles are preferentially contained in its larger particles 70-160 mkm.

3.1. Mineralogy

Mineralogy of the ore (Iberian pegmatite) (Figure 2) is dominated by quartz (39 wt.%), plagioclase (22 wt.%) and light mica (17 wt.%). K-feldspar, tourmaline, (Li)chlorite are present with a significantly lower proportion (<9% by weight). Spodumene is identified as well (Table 1), which is the most important Li carrier.

The presence of a large number of minerals makes identification difficult, as unresolvable overlays are registered. The proportion of the relevant constituents can be estimated from the observed intensities.

According to XRD-analysis, sanidine KAlSi$_3$O$_8$ and illite (K, H$_3$O)Al$_2$[(OH)$_2$AlSi$_3$O$_{10}$] are the main components, and SiO$_2$, CaCO$_3$, NaCl, CaSO$_4$·2H$_2$O, clinochlore (Mg, Fe^{2+})$_5$ Al(AlSi$_3$O$_{10}$)(OH)$_8$, bytownite (Ca, Na)[(Al,Si)$_4$O$_8$] are the minor components of the clay sample.

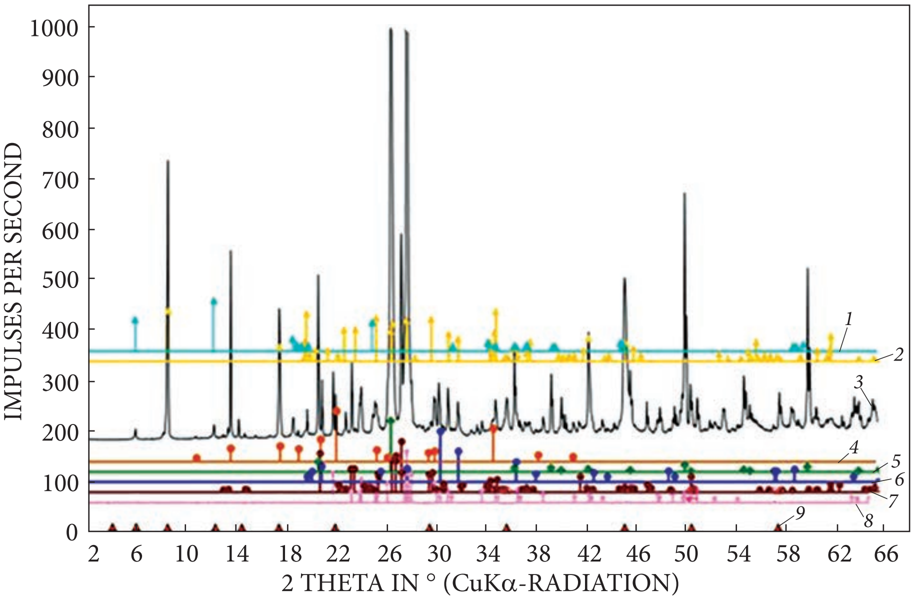

Fig. 2. Diffractograms of powders of minerals: *1* — chlorite, *2* — muscovite, *3* — Iberian pegmatite as a whole ore sample, *4* — tourmaline, *5* — quartz, *6* — spodumene, *7* — K-feldspar, *8* — plagioclase, *9* — d-values

3.2. Geochemistry

The outcrops and SRMs were analyzed for Ca, K, Na and Li by ICP-OES (iCAP 7000, Thermo Fisher) (Table 2). The certified standards show a very good recovery for the examined elements (±8%). Therefore, a highly quantitative analysis of silicates can be assumed.

3.3. Determination of lithium in different silicate ores and silicate minerals

Sample preparation involves sintering of a sample with chlorinating agent NH_4Cl and with $CaCO_3$. The principal chemistry of the method is given below.

$$Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + 2NH_4Cl + 4CaCO_3 \rightarrow \rightarrow 2LiCl + 4CaSiO_3 + Al_2O_3 + 2NH_3\uparrow + H_2O + 4CO_2\uparrow \quad (1)$$

$$CaCO_3 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3\uparrow + CO_2\uparrow + H_2O \quad (2)$$

$$Li_2SiO_3 + CaCl_2 \rightarrow CaSiO_3 + 2LiCl \quad (3)$$

$$CaCO_3 \rightarrow CaO + CO_2\uparrow \ (700—1100\ °C) \quad (4)$$

$CaCl_2$ forms a liquid phase at high temperatures, which facilitates the decomposition of silicates (Eq. 3). After the thermal treatment, the sintered ore material is leached with hot water. Lithium chloride is leached to an aqueous solution, which subsequently can be analyzed with state-of-the-art analytical instruments. As a sinter is leached with hot water, NaCl, LiCl, KCl and $CaCl_2$ are transferred into the solution during filtration. Mg^{2+} turns to MgO as a result of reaction with $Ca(OH)_2$. The next step of the investigation was to choose the right temperature mode, additives and the time of reaction. For this, we investigated sintering in the interval of temperatures from 900 to 1200 °C (Table 3).

Lithium chloride is an easily volatile compound at high temperature. The higher the temperature, the less LiCl we can determine later. Accordingly, to avoid losses of LiCl, it is a must to adjust precise temperature. The highest concentration of Li in the leaching solution is reached when the temperature of a muffle furnace sets up at 900 °C for 60-65 min. Recoveries of lithium using a high-form Platinum crucible with a lid are up 3700 ppm and 4260 ppm after sintering for 60 min and 65 min respectively. Recovery of lithium using a wide-form Platinum crucible with a lid is up 4570 ppm after sintering for 65 min. Increase in temperature as well as usage of $(NH_4)_2SO_4$ instead of NH_4Cl leads to decrease in concentration of Li in the solution. This result shows that lithium chloride is volatile and it could be easily lost at 1000 °C and that the nature of a chlorinating agent drastically

Table 1. **Estimated proportions of identified minerals (in weight %)**

Mineral phases	Iberian pegmatite	Mineral phases	Iberian pegmatite
Plagioclase	22	Tourmaline	5
K-feldspar	5	(Li)chlorite	3
Quartz	39	Spodumene	9
Muscovite	17		

Table 2. **Element content of ore (Iberian pegmatite, Spain) and quality assessment by including certified reference rocks, g/kg**

Sample	Ca	K	Li	Na
Iberian pegmatite	4.42	19.90	4.91	32.00
SY-2 found	57.50	39.55	0.108	32.60
SY-2 declared	56.90	36.90	0.100	32.00
Recovery, %	101.05	107.18	108.00	102.00
RGM-1 found	8.36	37.20	0.066	30.21
RGM-1 declared	8.30	36.80	0.070	30.50
Recovery, %	100.72	101.10	94.28	99.05

Table 3. **Method development**

No.	Mode		Concentration (Li), ppm
	°C	min	
1	300 900	30 60	3700
2	300 1050	30 60	2850
3	300 1150	30 90	136
4	300 1050	30 60	64 $(NH_4)_2SO_4$ instead of NH_4Cl
5	700 1000 1200	30 30 10	3560
6	300 900	30 65	4260
7	300 900	30 65	4570
8	300 800	30 60	3800

matters in the process. Therefore, the optimal chosen conditions are heating a sample at 300 °C — 30 min, then at 900 °C — 60-65 min.

Analysis of ore (Iberian pegmatite, Spain), clay (Nevada, the USA) and SRMs on the content of lithium is given in the Table 4. All results related to the analysis of Li in clay belong to the sample with moisture up to 4.60%.

We found $(4.42 \pm 0.10) \cdot 10^3$ ppm Li ($P = 95$, $n = 6$) in ore samples and $(1.091 \pm 0.027) \cdot 10^3$ ppm Li ($P = 95$, $n = 4$) in clay samples by sintering. RSD varies from 1.6 to 2.2% for different matrices. These values are similar to approaches with a sodium peroxide fusion ($(4.62 \pm 0.24) \cdot 10^3$ ppm) and direct analysis of geological materials $(4.57 \pm 0.36) \cdot 10^3$ for ore samples and $(1.04 \pm 0.09) \cdot 10^3$ ppm for clay samples. Lithium oxide content of 3.68% was determined in NIST sample SRM 183 (lepidolite) with RSD of 2.40% by sintering. Recovery of lithium oxide from SRM 183 is reached up to 92.2%.

Conducting research also provides an additional justification that performing the direct analysis of Li in powder using "PGS-DDP-BAES" complex facilitates determination of lithium in geological samples. RSDs in this case reach 6.5-7.0% that is quite good for the analysis of powder.

The calibration curve was created from the instrumental response "PGS-DDP-BAES" at 4602.825 Å to a set of standard reference materials CP-OCH-1 at a range of concentrations of lithium. It is possible to determine lithium in various geological samples in the range of concentrations (Li, %): from 0.50 to 6.26 and from 0.01 to 0.1.

The advantages of the plasma source of spectrum excitation (the plasma jet with high stability, the low detection limit, the absence of the impact effect of matrix) ensure high accuracy and sensitivity of the spectrochemical analysis of samples of any composition.

Researchers of the KIT analyzed two certified rock materials together with Iberian pegmatite applying strong acids for their digestion (Table 2). One of the certified rock materials was a syenite (SY-2), the other one was a rhyolite (RGM).

The highest concentration of Li in the sample — $(4.91 \pm 0.06) \cdot 10^3$ ppm was determined using a four-acid assay digestion. The recovery received for the SY-2 was a bit higher than the certified value, in detail it was 8% higher (Table 2). Digestive solutions of two certified rock materials were premeasured 7 times during the ICP-OES analysis. Recovery of Li for RGM-2 and for Sy-2 were measured up to 94.3%, and 108.1% respectively applying a four-acid assay digestion. The reason for the higher value might be related to the ICP-OES analysis. The standard deviation was 1.4%, therefore the method is highly precise. The mean however was also a bit higher as

Table 4. **Analysis of ore (Iberian pegmatite, Spain), clay (Nevada, the USA) and SRMs**

Method of analysis, place, country	Sample	Sample preparation	Li, ppm ($P = 95$)	RSD, %
ICP-OES K-UTEC, Germany	Iberian pegmatite	$CaCO_3 + NH_4Cl$, sintering	$(4.42 \pm 0.10) \cdot 10^3$ ($n = 6$)	2.2
	Clay		$(1.091 \pm 0.027) \cdot 10^3$ ($n = 4$)	1.6
	SRM 183, the USA, Lepidolite 4.12% Li_2O		$(1.71 \pm 0.06) \cdot 10^4$ ($n = 4$) 3.68% Li_2O Recovery 92.2%	2.40
ICP-OES KIT, Germany	Iberian pegmatite	$HNO_3 + HF +$ $+ HCl + HClO_4$, digestion	$(4.91 \pm 0.06) \cdot 10^3$ ($n = 7$)	1.4
	RGM-2, the USA 700 ppm Li		$(6.600 \pm 0.027) \cdot 10^2$ ($n = 7$) Recovery 94.2	1.4
	Sy-2, Canada 1000 ppm Li		$(1.080 \pm 0.013) \cdot 10^3$ ($n = 7$) Recovery 108.1	1.4
AES "PGS-DDP-BAES", (IGMOF of NAS of Ukraine), Ukraine	Iberian pegmatite	Direct solid analysis	$(4.57 \pm 0.36) \cdot 10^3$ ($n = 5$)	6.5
	Clay		$(1.04 \pm 0.09) \cdot 10^3$ ($n = 5$)	7.0
ICP-MS ALS, Spain	Iberian pegmatite	A sodium peroxide fusion	$(4.62 \pm 0.24) \cdot 10^3$ ($n = 4$)	3.3

it should be for Li. It looks like as if Li is slightly overestimated with the ICP-OES analysis.

Z. Hu et al. suggest to use a sodium peroxide fusion for complete recovery of lithium in pegmatites and jadarite [11]. Lithium hosted in these deposits can occur with economic grades of rare earths and other trace metals such as boron and cesium.

Different techniques require different quantities of samples for optimal use. In general, it is sufficient to use 0.5 g of sample for sintering and fusion. Smaller amount of any geological sample (0.2 g) is used if the direct analysis of lithium or four-acid digestion method are applied.

4. Conclusions

With the newly developed $CaCl_2$-methodology, we developed a safe, eco-friendly, and economically viable method that allows to extract lithium from a wide range of silicate ores and clays. The lithium concentration in such ores can then be analyzed in the resulting aqueous solution with standard ICP-OES analysis. "PGS-DDP-BAES" is a system that integrates combustion of solid samples in plasma with their analyses. This technique suits solid geological samples very well. With its simplicity, and relatively rapid procedures, 6.5-7.0% RSDs, the atomic-emission complex for spectrum analysis can be used for the routine analysis of lithium in many geological materials.

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Conflicts of Interest

The authors declare no conflict of interest.

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БЕЗПЕЧНЕ ТА ЕКОЛОГІЧНЕ ВИЗНАЧЕННЯ ЛІТІЮ В СИЛІКАТНИХ РУДАХ ЗА ДОПОМОГОЮ СПІКАННЯ ТА ОПТИЧНО-ЕМІСІЙНОЇ СПЕКТРОМЕТРІЇ З ІНДУКТИВНО ЗВ'ЯЗАНОЮ ПЛАЗМОЮ

Розроблено нові методики кількісного визначення літію в літійвмісних силікатних мінералах і глинах. Досліджено прямий аналіз літію в порошку з використанням атомно-емісійного спектрального аналітичного комплексу *PGS-DDP-BAES* і спікання як метод підготовки зразка з подальшим аналізуванням методом оптико-емісійної спектрометрії з індуктивно-зв'язаною плазмою (ІЗП-ОЕС). Установлено, що новий атомно-емісійний спектральний аналітичний комплекс краще використовувати для ефективного подолання складних матричних ефектів. Він дає змогу здійснювати пряме кількісне визначення літію в твердих зразках (рудах, глинах). Відносне стандартне відхилення у разі прямого визначення літію в порошку досягає 7,0 %. Для вилучення літію із силікатних руд і глин шляхом спікання було вивчено різні параметри, зокрема температуру спікання, час реакції та домішки. Результати показують, що оптимальна температура спікання з NH_4Cl і $CaCO_3$ становить приблизно 900 °C. Оптимальні умови вилучення літію такі: 300 °C (30 хв) і 900 °C (60 хв), за масового співвідношення руда : NH_4Cl : $CaCO_3$ як 1 : 1 : 8. У цих умовах вилучення літію досягає 92 %. Відносні стандартні відхилення для методу зі спіканням і подальшим аналізуванням методом ІЗП-ОЕС коливаються в інтервалі 1,7—2,2 %.

Ключові слова: силікатні руди, глини, пегматит, літій, спікання.