N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES OF GEOLOGY AND TECHNICAL SCIENCES
ISSN 2224-5278
Volume 5, Number 443 (2020), 214 – 220 **https://doi.org/10.32014/2020.2518-170X.123**

UDC 637.334; 579.61
MRSTI 68.05.31

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FTIR- SPECTROSCOPIC CHARACTERISTICS OF THE DZHAKSY-KLYCH DEPOSIT SALTS

Abstract. Kazakhstan is a country with an arid climate, where a number of salt lakes are located, where industrial production of edible salt is carried out. Due to the increase in the volume of salt production for export needs and the possibility of expanding the scope of its use for medical and cosmetic purposes, new layers and deposits of salt are being developed. The purpose of this study was to refine the characteristics of Dzhaksy-Klych Deposit salts using FTIR spectroscopy. The objects of the study were samples of salt-containing raw materials selected from different sites of Dzhaksy-Klych Deposit. Based on the conducted research, it can be predicted that when the Aral sea turns into a chloride salt lake, the main sediment will be sodium chloride, with additional formation of salt deposits from sodium sulfate, calcium or magnesium. The results obtained provide useful information about the mineralogical composition of the Aral sea region salts, which complements the knowledge about the composition of minerals. The results of FTIR analyses show that the samples of salts of lake Dzhaksy - Klych are represented by the following compositions: halite, astrakhanite, hexahydrate, gypsum, mirabilite, and the absence of toxic substances in the studied salt samples confirms their suitability for use in food, pharmaceutical and cosmetic purposes.

Key words: salt, Dzhaksy-Klych deposit, FTIR spectroscopy, chemical composition, compounds.

Introduction. According to Zholtayev G. Zh. et al. (2018) opinion, each field must be subjected to a comprehensive study to determine its position in the regional and local structures, study the material composition. Salt is one of the natural components that can accumulate in solid form near natural and artificial reservoirs. There are known studies related to the negative environmental impact on the environment, and in particular on the biodiversity of soil and water(Emerson J. B. et al., 2013). A direct correlation was established between the level of soil salinity and the quantitative and qualitative characteristics of water microflora (Canfora L. et al., 2017). The influence of various factors on the indicators of biological activity of saline soils was studied (Yazdanpanah, N. et al., 2016). On the other hand, salt is an important source of valuable components for the full functioning of human and animal life (Thompson L. J., 2018).

Weather and climatic conditions of Kazakhstan contribute to the formation of salt deposits almost throughout the state, so the volume of table salt in the regions of the Republic is distributed as follows, thousand tons, according to region: Kzyl-Orda -27383.0; Aktyubinsk-8267.0; Atyrau-1069000.0; Kustanay - 2012.0; Kokchetau -42509. 0; Pavlodar – 163447.0; Semipalatinsk -29728.0; Taldy - Kurgan - 627.0; South-Kazakhstan-3887.0; Dzhambul – 10040.0.

At the same time, due to a number of reasons, the Kzyl-Orda region, in particular the region of the Aral sea region, was undeservedly excluded from the list of regressive regions. Indeed, it is necessary to recognize that environmental problems occur in the Aral sea region (Kurbaniyazov et al., 2009). At present, the level of the Aral sea has decreased in comparison with the level of 1957. (then the absolute mark was 54 m) by more than 14 m. Its area has decreased from 66.5 thousand km^2 to about 36 thousand km^2, and its water volume has decreased from 1000 km^3 to 320 km^3. The salinity of the water during this time increased from 8 to 14 g/l to a value of 25-50 g/L. The area of the exposed bottom is approximately 3 million ha (Zavyalov et al., 2012). In the Aral sea region, dust and salt storms have become common. Every year, according to the space monitoring laboratory, about 72 million tons of salt is carried away by the wind outside the Aral sea region. The content of sulfates exceeds 31% (of the total amount of salts), and sodium chloride is only 54%. The ionic composition of the salts is as follows: sodium – from 2.83 to 13.73%; sulfate - ion - 7.5 – 30.14; calcium - up to 1.08; magnesium – 3.03; potassium – 0.93; carbonate - ion– 0.18; chlorine– 2.09; water– up to 55.23%.

Sea salt is extremely important for human nutrition, both for daily internal consumption and for external influences in the composition of therapeutic baths and cosmetic products. Salt minerals are actively involved in all the metabolic processes of our body (Lee & Lee, 2014). Therefore, salt is used for the prevention and treatment of many diseases (Kohlmeier M., 2015).

According to Internet resources, only in one quarter of the year, the volume of iodized salt production in Kazakhstan reaches 68.7 thousand tons. Every year, only the Kyzylorda region produces 66.9 thousand tons. The production of iodized salt is being increased by producers of the Zhambyl region: in the three months of 2019, 1.4 thousand tons were produced, despite the fact that in the same period of 2018, there was no salt production in the region at all. In the Turkestan region, salt production amounted to 0.4 thousand tons. Kazakhstan practically does not need to import salt: in January–February 2019, deliveries from abroad amounted to only 6.4% of resources (3 thousand tons). Kazakhstan's salt exports to foreign markets amounted to 35.9 thousand tons, an increase of 33.4% over the year. Salt is used mainly for food purposes, but such aspects of its use as use for medicinal or cosmetic purposes are not fully in demand. Despite the fact that the chemical compositions of the salts of most salt deposits in Kazakhstan are sufficiently studied, new areas and layers are being developed, the composition of which requires additional research and clarification. In this regard, the purpose of this study was to refine the characteristics of the Dzhaksy-Klych lake salts using Fourier-infrared spectroscopy.

Objects and methods of research. The objects of the study were samples of gold-containing raw materials selected from different points of Lake Dzhaksy-Klych.

Lake Dzhaksy-Klych –the biggest salt lake of the Caspian lowlands located in the Aral sea region. The lake is of marine origin and consists of two parts with an area of 18 and 58 km. The thickness of the salt deposit is about 2 m. Sampling was carried out in accordance with GOST 33770-2016. Samples were taken from the Dzhaksy-Klych Deposit by "Onyx-R" LLP and the authors of the article (table).

Description of Lake Dzhaksy-Klych samples

Sample	Sampling site (well No.)	Sampling depth, m	Coordinates (WGS 84)		pH	t, °C
			n.l.	e.l.		
1 (S1)	3s	0.0-0.5	46^{0} 56'3,38"	62^{0} 2'32.34"	7,3	25
2 (S2)	7s	0.6-1.1	46^{0} 55'53,09"	62^{0} 3'29.09"	7,2	25
3 (S3)	4s	0.6-1.1	46^{0} 56'0,81"	62^{0} 2'46.49"	7,3	26
4 (S4)	6s	1.2-1.3	46^{0} 55'55,66"	62^{0} 3'14.93"	7,1	27
8 (S5)	14s	1.5-2.0	46^{0} 56'7,71"	62^{0} 3'16.93"	7,2	27

Five different salts from Dżaksy-Klych Lake (sample 1, 2, 3, 4 and 8 denoted later as S1, S2, S3, S4, S5) were chosen for the further study (figure 1).

Figure 1 – Dried and milled salt samples

In the study of salt-containing raw materials, a mass spectrometer with inductively coupled plasma was used, the elements were determined in accordance with ST RK ISO 17294-2-2006. Chemical analysis was carried out according to GOST 13685-84. Research conditions: temperature-25^{0}C; humidity -83.0%; pressure-714 mm Hg.

FTIR spectroscopy: A Fourier transform infrared spectrometer (Cary 630, Agilent) was used to obtain the IR spectra. Spectra were collected in 4 cm^{-1} resolutions and coadded 100 scans. A 45-degree reflection-absorption optical accessory was used to perform the measurements. In this optical system, a gold-coated plate was used as a reflection reference. To remove the spectral interference from water absorption bands, samples S1, S2, S3, S4 and S5 were dried (100°C, 24 or 72h) before measuring the reflection-absorption IR spectra. Dried salts were placed on top of the gold-coated plate to obtain the reflection spectra. FTIR spectra were displayed in an ordinary absorption unit.

Statistical processing of the results was performed by calculating the arithmetic mean and the standard deviation. All determinations were carried out in 3-and 5-fold repetitions. The data was processed using an IBM Pentium personal computer based on Excel application software packages.

Results and discussion. FTIR studies of the salts help in the identification of minerals present in the salts. The coupled vibrations are appreciable due to availability of various constituents. In figure 2, FTIR spectra of all salts are shown.

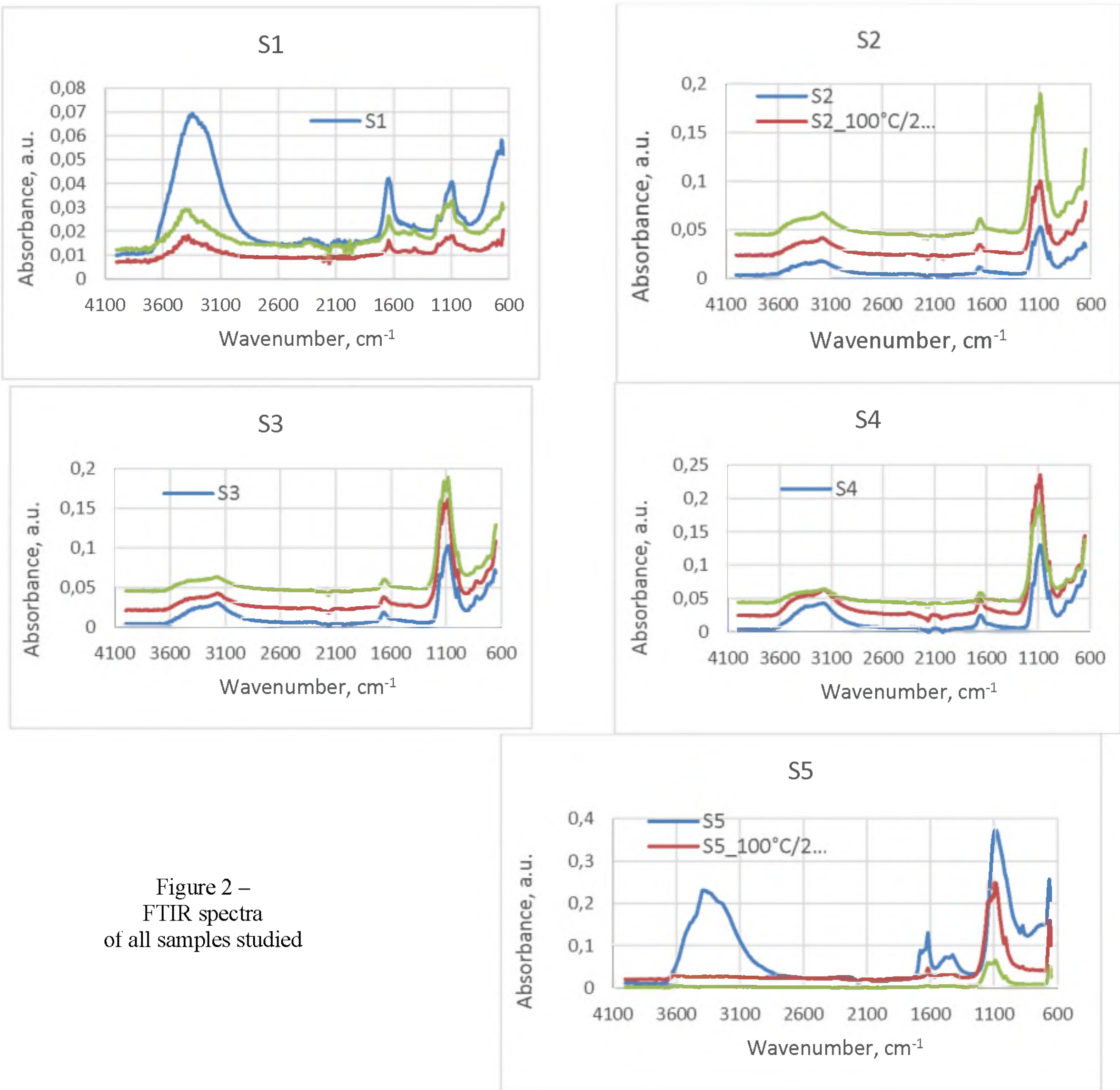

Figure 2 –
FTIR spectra
of all samples studied

In all samples, there are 3410 and 1635 cm^{-1} peaks. This peaks come from water in structure of sample. In other regions the following minerals were considered (Miller F.A., Wilkins Ch.H., 1952):

1. Sodium carbonate Na_2CO_3 700, 705, 855, 878, 1440, 1755, 2500, 2620 cm^{-1} peaks;
2. Calcium sulfate $CaSO_4$. $2H_20$ 667, 1010 , 1130, 1630, 1670, 2200, 3410 cm^{-1} peaks;
3. Sodium sulfate Na_2SO4 645, 1110 cm^{-1} peaks;
4. Sodium silicate 775, 832, 980, 1125, 1165, 1695, 2330, 3280 cm^{-1} peaks.

The sharp peak at ~1100 cm^{-1} was mainly assigned to such associated complexes of alkali and alkaline earth metals and SO_4^{2-}.The reference data is presented in figure 3.

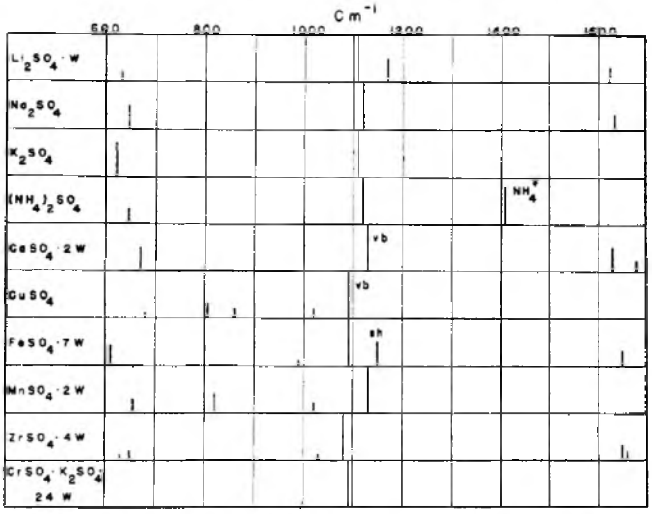

Figure 3 – Comparison of FTIR data for different sulfates (Miller F.A., Wilkins Ch.H., 1952)

Just as with sulfates, most other polyatomic ions exhibit characteristic frequencies. These are summarized in figure 4. However, it seems that mainly bands from sulfates are present.

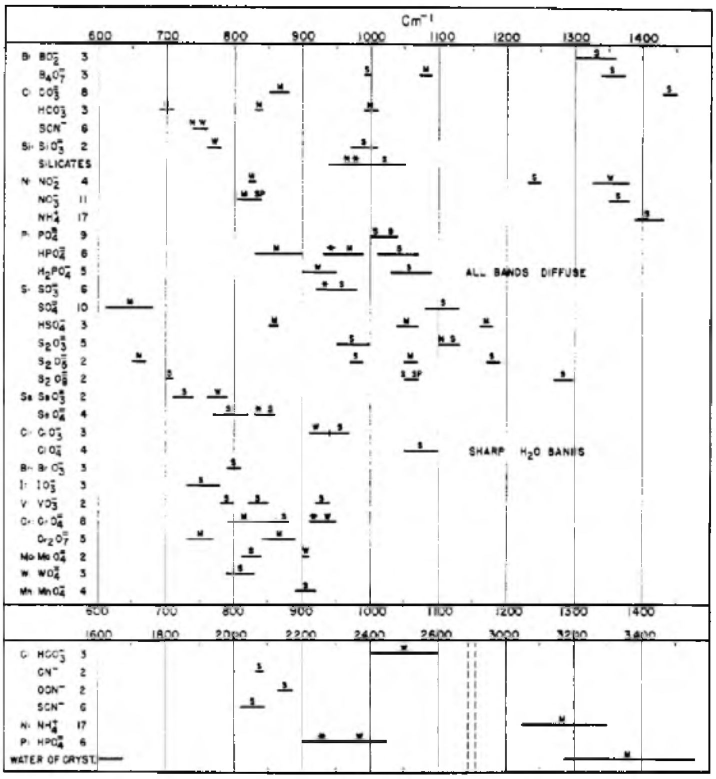

Figure 4 – Characteristic frequencies of polyatomic inorganic ions (Miller F.A., Wilkins Ch.H., 1952)

We can assume that with the transformation of the Aral Sea into a chloride salt lake, only NaCl will be deposited. Thus NaCl will be the main precipitate, whereas other salts will be minor. One can expect sodium (e.g. Na_2SO_4), calcium (e.g. $CaSO_4$) or magnesium salts ($MgSO_4$), and others.

The performed analyses provided useful information about the mineralogical composition of the salts. This is a fundamental step in gaining knowledge about the constituent of minerals.

Conclusions. The results of these studies give grounds for predicting that only NaCl will be deposited when the Aral sea turns into a chloride salt lake. Thus, NaCl will be the main precipitate, while other salts will be secondary. In addition, you can expect the formation of salt layers from sodium (for example, Na_2SO_4), calcium (for example, $CaSO_4$), magnesium ($MgSO_4$) and others. The analyses provided useful information about the mineralogical composition of the salts. This is a fundamental step in gaining knowledge about the composition of minerals. As a result of the conducted FTIR analyses, it was found that the samples of lake Dzhaksy -Klych salts are represented by the following compositions: halite, astrakhanite, hexahydrate, gypsum, mirabilite. The absence of toxic substances in the salt samples confirms their suitability for use in food, pharmaceutical and cosmetic purposes.

The work was carried out under the grant of the Ministry of education and science of the Republic of Kazakhstan AR05131728: "Development of production technology and obtaining prototypes of new cosmetic products based on pharmacological studies of domestic salt-containing and vegetable raw materials" (2018-2020).

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ЖАҚСЫ-КЛЫШ КЕН ОРНЫ ТҰЗЫНЫҢ ИҚ-ФУРЬЕ СПЕКТРОСКОПИЯЛЫҚ СИПАТТАМАСЫ

Аннотация. Қазақстан аридтік климатты мемлекет болып келеді, ас тұзын өнеркәсіпте өндіретін бірқатар тұзды көлі бар. Экспорттық қажеттіліктерге тұз өндірісінің ұлғаюы және оны емдік, косметологиялық мақсаттарға қолдану аясын кеңейту мүмкіндігіне байланысты жаңа қабаттар мен тұз шоғыры игерілуде. Қазақстанның ауа-райы мен климаттық жағдайы елде тұзды шөгінділердің пайда болуына ықпал етеді, сондықтан республика аймақтарындағы ас тұзы (мың тонна) келесідей бөлінеді: Қызылорда 27383,0; Ақтөбе 8267.0; Атырау 1069000.0; Қостанай 2012.0; Көкшетау 42509. 0; Павлодар 163447,0; Семей 29728,0; Талдықорған 627,0; Оңтүстік Қазақстан 3887,0; Жамбыл 10 040,0. Бірқатар себеп бойынша Қызылорда аймағы, атап айтқанда, Арал теңізі регрессивті аймақ тізімінен шығарылды. Шын мәнінде экологиялық проблемалар Арал маңында туындайтынын мойындау керек. Бұл зерттеудің мақсаты ИҚ-Фурье спектроскопия әдісімен Жақсы-Клыш кен орында тұз сипаттамаларын нақтылауды қамтиды. Зерттеу нысаны ретінде Жақсы-Клыш кен орындағы түрлі нүктеден таңдалған күкіртті шикізаттың 5 үлгісі алынды. Барлық сынамада галиттің бар екендігі анықталды. Астраханит тек 2,3 және 4 сынамада анықталады. 3 және 4 сынамада гексагидрат және гипс белгіленген. 4-сынамадан мирабилит табылды. Ауыр металдар мен улы заттар табылған жоқ, бұл осы қабат тұзын кеңінен қолдануға ұсынуға мүмкіндік береді. Зерттеу нәтижелері Арал теңізі хлоридті тұзды көлге айналған кезде тек NaCl шөгетінін көрсетті. Сонымен, NaCl негізгі шөгінді, ал қалған тұздар екінші реттік болады. Сонымен қатар, натрийден (мысалы, Na2SO4), кальцийден (мысалы, CaSO4), магнийден (MgSO4) және басқалардан тұз қабаты пайда болады деп болжанады. Талдау жұмыстары тұздың минералогиялық құрамы туралы пайдалы ақпарат берді. Бұл – минералды негіз алудың іргелі қадамы. FTIR көлін талдау нәтижесінде Жақсы-Кылыч ұсынған тұз сынамалары келесі композиция арқылы ұсынылатындығы анықталды: галит, астраханит, гексахидрат, гипс, мирабилит. Тұз сынамасында улы заттардың болмауы олардың тағамдық, фармацевтикалық және косметикалық мақсаттарда қолдануға жарамдылығын көрсетеді.

Түйін сөздер: тұз, Жақсы-Кылыч кен орны, ИҚ-Фурье спектроскопиясы, химиялық құрамы, қосылыстар.

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ИК-ФУРЬЕ СПЕКТРОСКОПИЧЕСКАЯ ХАРАКТЕРИСТИКА СОЛЕЙ МЕСТОРОЖДЕНИЯ ДЖАКСЫ-КЛЫЧ

Аннотация. Казахстан является государством с аридным климатом, где расположен ряд соленых озер, где производится промышленная добыча пищевой соли. В связи с увеличением объемов добычи соли на экспортные нужды и возможностью расширения сферы ее применения в лечебных и косметологических целях осваиваются новые пласты и залежи соли. Погодно-климатические условия Казахстана способствуют формированию солевых отложений практически на всей территории страны, поэтому объем поваренной соли в регионах республики распределяется следующим образом, тыс. тонн по регионам: Кзыл-Ординская - 27383,0; Актюбинск-8267.0; Атырау-1069000.0; Костанай - 2012,0; Кокшетау - 42509. 0; Павлодар - 163447,0; Семей -29728,0; Талдыкорган -627,0; Южно-Казахстанская-3887,0; Жамбыл - 10040,0. При этом по ряду причин Кзыл-Ординский регион, в частности район Приаралья был незаслуженно исключен из списка регрессивных регионов. Необходимо признать, что экологические проблемы возникают в районе Аральского моря. Целью данного исследования было уточнение характеристик солей озера Джаксы-Клыч методами ИК-Фурье спектроскопии. Объектами исследования послужили 5 образцов солесодержащего сырья, отобранных из разных точек озера Джаксы-Клыч. Было установлено, что во всех пробах присутствует галит. Астраханит выявлен только в пробах 2,3 и 4. В пробах 3 и 4 отмечены гексагидрат и гипс. В пробе 4 обнаружен мирабилит. Тяжелые металлы и токсичные вещества обнаружены не были, что позволяет рекомендовать соли данных пластов для широкого применения. Результаты этих исследований дают основание прогнозировать, что только NaCl будет откладываться, когда Аральское море превратится в хлоридное соленое озеро. Таким образом, NaCl будет основным осадком, а другие соли - вторичными. Кроме того, можно ожидать образования слоев соли из натрия (например, Na2SO4), кальция (например, CaSO4), магния (MgSO4) и других. Анализ предоставил полезную информацию о минералогическом составе солей. Это фундаментальный шаг в получении знаний о составе минералов. В результате проведенных FTIR-анализов установлено, что образцы солей озера Джаксы-Клыч представлены следующими составами: галит, астраханит, гексагидрат, гипс, мирабилит. Отсутствие токсичных веществ в образцах солей подтверждает их пригодность для использования в пищевых, фармацевтических и косметических целях.

Ключевые слова: соль, месторождение Джаксы-Клыч, ИК-Фурье спектроскопия, химический состав, соединения.

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