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BIS(2,2,2-TRIFLUOROETHYL)(2-CYANOETHYL) PHOSPHATE – A NEW URANIUM EXTRAGENT

Abstract. Organophosphate compounds are widely used in industrial hydrometallurgical processes as extractants and complexones of non-ferrous, noble, rare-earth metals and transuranic elements. Among these compounds, organic phosphates occupy a special place, as they allow for the extraction processes with good selectivity and efficiency. However, a significant drawback of known organic phosphates is their low extraction capacity, as well as rather good solubility in water and their hydrolysability in aqueous acidic solutions, which leads to both loss of the extractant and contamination of the extracted metal with organophosphorus compounds. Therefore, the search and development of new uranium effective extractants is an important task for the development of modern hydrometallurgical processes.This report describes the successful use of available bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate, which is easily obtained from bis(2,2,2-trifluoroethyl) chlorophosphate and 3-hydroxypropanonitrile in the pyridine/diethyl ether system as an extractant of uranium from uranium-containing acid solutions. For this functional phosphate containing a cyano group, one should expect a synergistic effect of the extraction properties of the phosphates themselves, as well as of the known extractants - contribute to an increase in its incombustibility.The purpose of this research is to develop the optimal conditions for the scaled synthesis of bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate, to accumulate its enlarged batch and to study the extraction properties in the production process of uranium extraction from uranium-containing sulfate and nitric acid solutions.The research results showed that bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate, easily obtained from the available bis(2,2,2-trifluoroethyl) chlorophosphate and 3-hydroxypropanonitrile in the pyridine/diethyl ether system, exhibits pronounced extraction properties with respect to uranium. Thus, the use of this extractant in the production of the extraction of uranium from uranium-containing nitric acid or sulfuric acid solutions was 20.7% and 18.7%; the content of uranium in the extractant was 63.9 g/dm^3 and 49. 7 g/dm^3, respectively.Positive results were also obtained when studying the synergistic properties of the new extractant and the traditional - bis(2-ethylhexyl) phosphate. Using a mixture of these extractants (their weight ratio was 1:1.2) allows you to extract 57% of uranium from the uranium sulphate solution. This is 9% more than in a similar process using only bis(2-ethylhexyl) phosphate as an extractant. The use of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate as a new extractant makes it possible to extract up to 20.7% of uranium from technological nitrate or sulphate of uranium-containing solutions. With the combined use of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate and the known extractant bis(2-ethylhexyl) phosphate in this process, a synergistic effect is observed, which increases the efficiency of uranium extraction and improves the technological indicators of extraction.The extractantbis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate works more efficiently in nitric acid solutions than in sulphate.

Keywords: organic phosphates, polyfluoroalkyl groups, extractant, uranium.

Introduction. Organophosphate compounds are widely used in industrial hydrometallurgical processes as extractants and complexones of non-ferrous, noble, rare-earth metals and transuranic elements [1-7]. Among these compounds, organic phosphates occupy a special place, as they allow for the extraction processes with good selectivity and efficiency [1, 2, 4-8]. For example, tributyl phosphate in most countries, including Russia and Kazakhstan, is used in hydrometallurgy to determine and separate heavy metals (including uranium) [1, 4–10], as well as to separate uranium from nuclear fuel. 2 There are patent data on the use of bis(2-ethylhexyl) phosphate (the trivial name of the extractant is di(2-ethylhexyl) phosphoric acid) in the mixture as an extractant of uranium from industrial ores of Kazakhstan [9]. However, a significant drawback of known organic phosphates is their low extraction capacity, as well as rather good solubility in water and their hydrolysability in aqueous acidic solutions, which leads to both loss of the extractant and contamination of the extracted metal with organophosphorus compounds [2, 12]. Therefore, the search and development of new uranium effective extractants is an important task for the development of modern hydrometallurgical processes.

This report describes the successful use of available bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate, which is easily obtained from bis(2,2,2-trifluoroethyl) chlorophosphate and 3-hydroxypropanonitrile in the pyridine/diethyl ether system [13] as an extractant of uranium from uranium-containing acid solutions. For this functional phosphate containing a cyano group, one should expect a synergistic effect of the extraction properties of the phosphates themselves, as well as of the known extractants - contribute to an increase in its incombustibility [14-19].

The purpose of this research is to develop the optimal conditions for the scaled synthesis of bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate, to accumulate its enlarged batch and to study the extraction properties in the production process of uranium extraction from uranium-containing sulfate and nitric acid solutions.

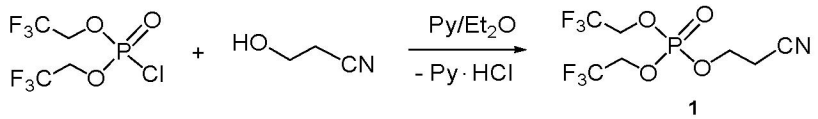
Methods and Materials. As extractants used bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate 1, specially synthesized under the conditions of scaled synthesis (see below), and commercial bis(2-ethylhexyl) phosphate 2 (initial content of the main component 70 %), «Khimprom» (Extragent 57, grade A), TC 2435-337-065763441-2004, density 0.945 g/cm^3.

As a source of raw materials used sulfuric acid solution of marketable desorbate from uranium production with a uranium concentration of 15.0 g/dm^3 (concentration of H_2SO_4 – 26.95 g/dm^3), as well as a nitric acid solution of commercial desorbate with a uranium concentration of 15.0 g/dm^3 (concentrationHNO_3 - 52.50 g/dm^3). As a diluent for extraction, commercial diesel fuel produced by JSC PPCP (Pavlodar Petrochemical Plant), GOST 10227-86, density 0.776 g/cm^3 was used.

The ^{1}H, ^{13}C, ^{19}F, ^{31}PNMR spectra were obtained on a Bruker DPX 400 spectrometer (400.13, 101.61, 376.50 and 161.98 MHz, respectively) in a $CDCl_3$ solution, the internal standard is HMDS (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), the external standard is 85% H_3PO_4 (^{31}P). IR spectra were recorded on a Bruker IFS 25 spectrometer in a thin layer.

The concentration of the main component - uranium in aqueous solutions and the organic phase was determined by the bulk method - titration with ammonium vanadate [20].

*Enlarged synthesis of the extractant bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate 1.*Bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate was obtained in a yield of 80% by the interaction of bis(2,2,2 trifluoroethyl) chlorophosphate with 3-hydroxypropanonitrile in the pyridine (Py)/diethyl ether system (Scheme).



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Scheme - The reaction for the production of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate

Previously, to obtain this extractant, 30 mmol of the starting chlorophosphate was used [13], in this report the method of scaled (3 times) synthesis of the preparation of the target compound **1** was developed.

The method of integrated synthesis of extractant bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate 1. In a three-necked flask equipped with a reflux condenser and a dropping funnel, a solution of 25.24 g (90 mmol) bis(2,2,2-trifluoroethyl) chlorophosphate in 180 ml of absolute diethyl ether. To the resulting

solution was added dropwise with stirring a solution of 6.40 (90 mmol) of 3-hydroxypropanonitrile and 7.12 g (90 mmol) of pyridine in 20 ml of diethyl ether for 1 hour at room temperature, while the formation of a white precipitate of pyridinium hydrochloride was observed.The reaction mixture was stirred at room temperature for an additional 8 hours and left overnight. The pyridinium hydrochloride precipitate was filtered and washed with diethyl ether (3x30 ml). The solvent from the filtrate was distilled off under reduced pressure, the residue was distilled in vacuo. Received 21.5 g (80%) of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate 1, clear liquid, BP 129-130 °C (1 mmHg.), Lit. data 129 °C (1 mmHg) [13], d_4^{20} 1.5191. Found, %: C 26.34; H 2.27; F 36.49; N 4.39; P 10.11. $C_7H_8F_6NO_4P$. Calculated,%: C 26.68; H 2.56; F 36.18; N 4.45; P 9.83. The spectral characteristics are identical to the literary ones [13].

General method of uranium extraction from uranium-containing acid solutions. Tests were carried out under various conditions of the organization of the extraction process in the parameters as close as possible to the production ones. The process of extracting uranium was investigated from uranium sulfate solutions: extractant **1**, a mixture of extractants **1** + **2** and extractant **2**, from uranium nitrate solutions: extractant **1.**

At the first stage of work, an extraction mixture was prepared, which included diesel fuel (diluent) and extractants with a concentration in the extraction mixture of 7%. In the experiment using a mixture of extractants of bis(2,2,2-trifluoroethyl) (2-cyanoethyl) phosphate **1** and bis (2-ethylhexyl) phosphate **2**, a weight ratio of components 1.0:1.2 was taken. The diluent is used to increase the speed of phase separation, stabilize and prevent significant losses of the extractant, as well as to increase the yield and reduce the viscosity of the extractant.

At the second stage of the work, the prepared extraction mixture (diluent and extractant) was added to aqueous solutions of sulphate or nitric acid product strips. The extraction of uranium was carried out by a single contact of the organic and aqueous phases with constant stirring on a magnetic stirrer (the temperature in the production room is 24 °C, the contact time is 20 min). In the case of product sulfate desorbate, the ratio of organic and aqueous phases used (O:B) used in production was selected: 1.0:17.33; in the case of product nitrate desorbate, extraction was carried out at a ratio O:B of 1.0:20.8. Under laboratory conditions, separation funnels were used to separate the phases.

Extraction of uranium from sulfate or uranium-containing nitrate solutions of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate 1 was carried out under the above conditions and showed that extractant **1** is poorly soluble in diesel fuel. As a result, at the final stage of extraction, three phases were obtained with the following uranium content in them: the lower phase — extractant 1, the uranium content 49.7 g/dm^3 (in the case of sulfuric acid solutions) or 63.9 g/dm^3 (using nitric acid solutions); middle phase - extraction mother liquor, uranium content 12.2 g/dm^3 (in the case of sulphate solutions) or 11.9 g/dm^3 (using nitric acid solutions); the upper phase is diesel fuel, the uranium content is 0.0 g/dm^3 (i.e., there was no participation in the extraction process). Extraction of uranium with extractant **1** was: 20.7% (from a nitric acid solution) and 18.7% (from a sulfate solution).

Extraction of uranium from uranium sulfate solutions with a mixture of extractants - bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate 1 and bis(2-ethylhexyl)phosphate 2. As a result of extraction at the final stage, three phases were obtained with the following uranium content in them: the lower phase - extractant **1**, the uranium content 1.7 g/dm^3; middle phase - extraction liquor, uranium content 6.45 g/dm^3; the upper phase is diesel fuel and extractant **2**, the uranium content is 10.6 g/dm^3. Extraction of uranium with a mixture of extractants **1** and **2** was 57%.

Extraction of uranium from uranium sulfate solutions of bis(2-ethylhexyl) phosphate 2. As a result of extraction, at the final stage, two phases were obtained with the following uranium content in them: the lower phase - extraction mother liquor, the uranium content of 7.8 g/dm^3; the upper phase is diesel fuel and extractant **2**, the uranium content is 8.4 g/dm^3. The formation of the third phase in this case did not occur. Extraction of uranium extractant **2** was 48%.

To study the extraction properties of bis(2,2,2-trifluoroethyl)(2-cyanoethyl)phosphate in the process of extracting uranium from marketable desorbates of uranium-containing sulphate and nitrate solutions, an enlarged batch of this extractant from bis(2,2,2-trifluoroethyl) chlorophosphate was accumulated and 3-hydroxypropanonitrile under scaled synthesis conditions. For the synthesis, 3-hydroxypropanonitrile (Alfa Aesar) (purity 97%) was used; the initial bis(2,2,2-trifluoroethyl) chlorophosphate was obtained according to a known procedure [13].

Results and discussion. The research results showed that bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate **1**, easily obtained from the available bis(2,2,2-trifluoroethyl) chlorophosphate and 3-hydroxypropanonitrile in the pyridine/diethyl ether system, exhibits pronounced extraction properties with respect to uranium. Thus, the use of this extractant in the production of the extraction of uranium from uranium-containing nitric acid or sulfuric acid solutions was 20.7% and 18.7%; the content of uranium in the extractant **1** was 63.9 g/dm^3 and 49. 7 g/dm^3, respectively (table, experiments 1 and 2).

Positive results were also obtained when studying the synergistic properties of the new extractant **1** and the traditional [9] - bis(2-ethylhexyl) phosphate **2**. Using a mixture of these extractants (their weight ratio was 1:1.2) allows you to extract 57% of uranium from the uranium sulphate solution. This is 9% more than in a similar process using only bis(2-ethylhexyl) phosphate **2** as an extractant (table, cf. experiments 3 and 4).

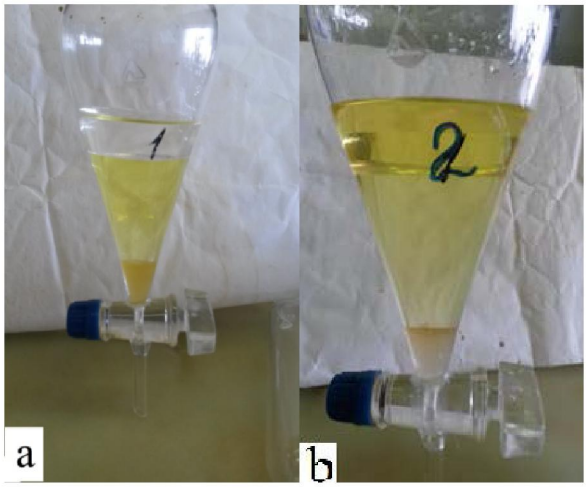

Figure 1 - Extraction of uranium using bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate (a),
using the mixture of uranium bis (2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate and bis(2-ethylhexyl) phosphate (b)

Table - The results of determining the content of uranium in the extraction products from acid solutions of commodity desorbate[a]

№ experience	Extragents**1** and **2**	Extraction of uranium from solution, %
1	Extragent**1**	20.7 (63.9)[b]
2	Extragent**1**	18.7 (49.7)[b]
3	Extragent**1** + Extragent**2**[b]	57.0
4	Extragent**2**	48.0

[a]In experiment № 1, uranium-containing nitrate solution was used as a raw material; in experiments № 2-4 - uranium sulfate solutions. [b]In brackets - the uranium content in the extractant 1, g/dm^3. in the weight ratio of extractants **1** and **2** = 1:1.2.

Thus, the conditions for the enhanced synthesis of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate **1** based on the reaction of bis(2,2,2-trifluoroethyl)chlorophosphate and 3-hydroxypropanonitrile in the pyridine/diethyl ether system have been worked out. an experimental batch of phosphate **1** and studied its extraction properties with respect to uranium.

Conclusion

1. The use of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate as a new extractant makes it possible to extract up to 20.7% of uranium from technological nitrate or sulphate of uranium-containing solutions.

2. With the combined use of bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate and the known extractant bis(2-ethylhexyl) phosphate in this process, a synergistic effect is observed, which increases the efficiency of uranium extraction and improves the technological indicators of extraction.

3. The extractant bis(2,2,2-trifluoroethyl)(2-cyanoethyl) phosphate works more efficiently in nitric acid solutions than in sulphate.

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БИС(2,2,2-ТРИФТОРЭТИЛ)(2-ЦИАНОЭТИЛ)ФОСФАТ - УРАННЫҢ ЖАҢА ЭКСТРАГЕНТІ

Аннотация. Фосфор органикалық қосылыстар өнеркәсіптік гидрометаллургиялық процестерде түсті, асыл, сирек-жер металдарының және трансурандық элементтердің экстрагенттері және комплексондары ретінде кеңінен қолданылады. Бұл қосылыстардың ішінде органикалық фосфаттар ерекше орын алады, өйткені олар экстракция процестерін жақсы таңдамалықпен және тиімділікпен жүргізуге мүмкіндік береді. Алайда белгілі органикалық фосфаттардың маңызды кемшілігі олардың экстракциялық қабілеттілігінің төмендігі, сонымен қатар суда ерігіштігі және сулы қышқыл ерітінділеріндегі гидролизі болып табылады, бұл экстрагенттің жоғалуына да, алынған металдың фосфор органикалық қосылыстарымен ластануына әкеледі. Сондықтан уранның жаңа тиімді экстрагенттерін іздеу және оны әзірлеу қазіргі гидрометаллургиялық процестерді дамытудың өзекті міндеті болып табылады.Бұл жариялымда қолжетімді бис(2,2,2-трифтороэтил) (2-цианоэтил) фосфатты, бистен(2,2,2-трифторэтил) оңай алынатын хлор фосфатты және пиридин/диэтил эфир жүйесіндегі 3-гидроксипропанонитрилді құрамында уран бар қышқыл ерітінділерінен уран экстрагенті ретінде пайдалану туралы мәліметтер келтірілген. Құрамында тобы бар функционалды фосфат үшін фосфаттардың және олардың белгілі экстрагенттері - цианидтердің экстракциялық қасиеттерінің синергетикалық әсерін күту керек. Сонымен қатар, бұл экстрагентте полифторалкил топтарының болуы оның үйлесімсіздігінің артуына ықпал етуі керек.

Бұл зерттеудің мақсаты - бис (2,2,2-трифлороэтил) (2-цианоэтил) фосфаттың кеңейтілген синтезі үшін оңтайлы жағдайларды жасау, оның үлкейтілген партиясын шығару және уран сульфаты мен азот қышқылының ерітінділерінен уран алудың өндірістік процесінде экстракциялық қасиеттерді зерттеу. Зерттеу нәтижелері қол жетімді жариялымда қолжетімді бис(2,2,2-трифтороэтил) (2-цианоэтил) фосфатты, бистен(2,2,2-трифторэтил) оңай алынатын хлор фосфатты және пиридин/диэтил эфир жүйесіндегі 3-гидроксипропанонитрилді уранға қатысты айқын экстрациондық қасиеттер көрсетеді (1а-сурет). Сонымен, бұл экстрагентті құрамында уран бар азот немесе сульфат ерітінділерінен уран алудың өндірістік процесінде қолдану 20,7% және 18,7% құрады; экстрагентте уран мөлшері сәйкесінше 63,9 г/дм^3 және 49,7 г/дм^3 құрады.. Дәстүрлі - бис (2-этилексил) фосфатын және жаңа экстрагенттің синергетикалық қасиеттерін зерттеу кезінде оң нәтижелер алынды. Бұл экстрагенттердің қоспасын қолдану (салмақ коэффициенті 1: 1,2) құрамында уран бар сульфат ерітіндісінен 57% уран алуға мүмкіндік береді. Бұл экстрагент ретінде тек бис (2-этилегексил) қолданған ұқсас процестен 9% артық.

Бис (2,2,2-трифлороэтил) (2-цианоэтил) фосфатын жаңа экстрагент ретінде пайдалану технологиялық азот қышқылы немесе құрамында уран бар сульфат ерітінділерінен 20,7% уран алуға мүмкіндік береді. Осы процессте бис (2,2,2-трифлороэтил) (2-цианоэтил) фосфаты және белгілі экстрагент бис (2-этилгексил) фосфатын қолданған кезде синергетикалық әсер байқалады, бұл уран алудың тиімділігін арттыруды қамтамасыз етеді және өндірудің технологиялық параметрлерін жақсартады. Бис (2,2,2-трифлороэтил) (2-цианоэтил) фосфат экстрагенті күкірт қышқылының ерітінділеріне қарағанда азот қышқылының ерітінділерінде тиімді жұмыс істейді.

Түйін сөздер: органикалық фосфаттар, полифторалкил топтары, экстрагент, уран

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БИС(2,2,2-ТРИФТОРЭТИЛ)(2-ЦИАНОЭТИЛ)ФОСФАТ - НОВЫЙ ЭКСТРАГЕНТ УРАНА

Аннотация. Фосфорорганические соединения широко применяются в промышленных гидрометаллургических процессах как экстрагенты и комплексоны цветных, благородных, редкоземельных металлов и трансурановых элементов. Среди этих соединений органические фосфаты занимают особое место, так как они позволяют проводить экстракционные процессы с хорошей избирательностью и эффективностью. Однако существенным недостатком известных органических фосфатов является их невысокая экстракционная способность, а также довольно хорошая растворимость в воде и их гидролизуемость в водных кислых растворах, что приводит как к потере экстрагента, так и к загрязнению экстрагируемого металла фосфорорганическими соединениями. Поэтому поиск и разработка новых эффективных экстрагентов урана является актуальной задачей развития современных гидрометаллургических процессов.В настоящем сообщении приводятся данные об успешном использовании доступного бис(2,2,2-трифторэтил)(2-цианоэтил)фосфата, легко получаемого из бис(2,2,2-трифторэтил)- хлорфосфата и 3-гидроксипропанонитрила в системе пиридин/диэтиловый эфир в качестве экстрагента урана из урансодержащих кислотных растворов. Для этого функционального фосфата, содержащего цианогруппу, следует ожидать синергизм действия экстракционных свойств самих фосфатов, а также известных экстрагентов – цианидов. Кроме того, наличие полифторалкильных групп в данномэкстрагенте должно способствовать повышению его негорючести.

Цель данного исследования - отработка оптимальных условий масштабированного синтеза бис(2,2,2-трифторэтил)(2-цианоэтил)фосфата, наработка его укрупненной партии и изучение экстракционных свойств в производственном процессе экстракции урана из урансодержащих сернокислых и азотнокислых растворов. Результаты исследования показали, что бис(2,2,2-трифторэтил)(2-цианоэтил)фосфат, легко получаемый из доступных бис(2,2,2-трифторэтил)хлорфосфата и 3-гидроксипропанонитрила в системе пиридин/диэтиловый эфир, проявляет выраженные экстракционные свойства по отношению к урану (рисунок 1а). Так, использование этого экстрагента в производственном процессе экстракции урана из урансодержащих азотнокислых или сернокислых растворов составило 20.7% и 18.7%; при этом содержание урана в экстрагенте было 63.9 г/дм^3 и 49.7 г/дм^3, соответственно. Положительные результаты были получены также при изучении синергетических свойств нового экстрагента и традиционного - бис(2-этилгексил)фосфата. Использование смеси этих экстрагентов (их весовое соотношение составляло 1:1.2) позволяет извлекать 57% урана из сернокислого урансодержащего раствора. Это на 9% больше, чем в аналогичном процессе с применением в качестве экстрагента только бис(2-этилгексил).

Применение бис(2,2,2-трифторэтил)(2-цианоэтил)фосфата в качестве нового экстрагента позволяет извлекать до 20.7% урана из технологических азотнокислых или сернокислых урансодержащих растворов. При комбинированном использовании в этом процессе бис(2,2,2-трифторэтил)(2-цианоэтил)фосфата и известного экстрагента - бис(2-этилгексил)фосфатанаблюдается синергетический эффект, обеспечивающий повышение эффективности извлечения урана и улучшающий технологические показатели экстракции. Экстрагент бис(2,2,2-трифторэтил)(2-цианоэтил)фосфат работает более эффективно в азотнокислых растворах, чем в сернокислых.

Ключевые слова: органические фосфаты, полифторалкильные группы, экстрагент, уран.

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