Effect of aluminum on the potentiometric determination of fluorine in spent lithium-ion battery black mass

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Fluorine is a significant component of the black mass of spent lithium-ion batteries (LIBs), occurring in residual electrolyte salts, their transformation products, fluorine-containing additives, and the polyvinylidene fluoride (PVDF) binder. The differing chemical nature of these components complicates quantitative fluorine determination in industrial black mass. In this work we examined the feasibility of separately assessing the water-extractable and residual, water-non-extractable fluorine fractions by direct potentiometry with a fluoride-selective electrode. Industrial black mass containing a mixture of cathode materials predominantly of the $LiNi_{1-x-y}Co_xAl_yO_2$ (NCA) type was treated by water leaching, acid leaching, and direct alkaline fusion in a NaOH–KOH mixture. The water-extractable fraction amounted to (2.33 ± 0.06) wt.%, whereas acid leaching and direct alkaline fusion of the as-received material both underestimated the fluorine content, indicating a matrix effect of aluminium during sample preparation. On a model sample of pure PVDF, alkaline fusion efficiently converted covalently bound fluorine into a form accessible to potentiometric determination. The critical factor proved to be the transfer of Al into solution followed by its possible precipitation upon pH adjustment, which partially removes fluoride from the dissolved, measurable form. The water-extractable fraction can therefore be determined with good repeatability, whereas quantification of the water-non-extractable fraction after alkaline decomposition is substantially compromised by Al-induced fluoride loss during neutralisation. This effect of aluminium – present in real black mass both within the cathode material and as metallic impurities – must be taken into account when developing analytical protocols for fluorine determination in LIB black mass.

Keywords: lithium-ion batteries; black mass; fluorine; fluoride-selective electrode; direct potentiometry; alkaline fusion; PVDF; $LiPF_6$; recycling.

Пайдаланылған литий-ионды аккумуляторлардың қара массасындағы фторды потенциометриялық анықтауға алюминийдің әсері

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Фтор – пайдаланылған литий-ионды аккумуляторлар (ЛИА) қара массасының маңызды құрамдас бөлігі; ол қалдық электролит тұздарының, олардың түрлену өнімдерінің, құрамында фторы бар қоспалардың және поливинилиденфторид (ПВДФ) полимер байланыстырғышының құрамында кездеседі. Бұл компоненттердің химиялық табиғатының әртүрлілігі өнеркәсіптік қара массадағы фторды сандық анықтауды қиындатады. Осы жұмыста фторид-селективті электродпен тікелей потенциометрия әдісі арқылы сумен экстракцияланатын және сумен экстракцияланбайтын қалдық фтор фракцияларын бөлек бағалау мүмкіндігі зерттелді. |Негізінен $LiNi_{1-x-y}Co_xAl_yO_2$ (NCA) типі басым катодтық материалдар қоспасынан тұратын өнеркәсіптік қара массаны талдау үшін сумен және қышқылмен шаймалау, сондай-ақ NaOH–KOH қоспасында тікелей сілтілік балқыту қолданылды. Сумен экстракцияланатын фтор фракциясының мөлшері (2,33 ± 0,06) мас.% құрады. Сонымен қатар, бастапқы қара массаны қышқылмен шаймалау және тікелей сілтілік балқыту анықталатын фтор мөлшерінің төмендеуіне әкелді, бұл сынама дайындау сатыларында алюминийдің матрицалық әсерін көрсетті. Таза ПВДФ модельдік үлгісінде сілтілік балқытудың коваленттi байланысқан фторды потенциометриялық анықтауға қолжетімді түрге тиімді ауыстыратыны көрсетілді. Шешуші фактор ретінде Al-дың ерітіндіге өтуі және оның кейіннен pH түзету кезінде тұнбаға түсуі анықталды; бұл фторидтің еріген, анықталатын түрінен ішінара шығарылуымен қатар жүреді. Сумен экстракцияланатын фтор фракциясын тікелей потенциометрия әдісімен жақсы қайталанғыштықпен анықтауға болады, ал сумен экстракцияланбайтын фракцияны сілтілік ыдыратудан кейін сандық бағалау бейтараптандыру кезінде Al әсерінен туындайтын фторидтің жоғалуы салдарынан айтарлықтай қиындайды. Нақты қара массада катодтық материалдың құрамында да, металдық қоспа түрінде де кездесетін алюминийдің анықталған әсерін ЛИА қара массасындағы фторды анықтаудың аналитикалық хаттамаларын әзірлеу кезінде ескеру қажет.

Түйін сөздер: литий-ионды аккумуляторлар; қара масса; фтор; фторид-селективті электрод; тікелей потенциометрия; сілтілік балқыту; ПВДФ; $LiPF_6$; қайта өңдеу.

Влияние алюминия на потенциометрическое определение фтора в чёрной массе отработанных литий-ионных аккумуляторов

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Фтор является значимым компонентом чёрной массы отработанных литий-ионных аккумуляторов (ЛИА) и присутствует в составе остаточных электролитных солей, продуктов их превращений, фторсодержащих добавок и полимерного связующего поливинилиденфторида (ПВДФ). Различная химическая природа этих компонентов осложняет количественное определение фтора в промышленной чёрной массе. В настоящей работе исследована возможность раздельной оценки водоэкстрагируемой и остаточной, неэкстрагируемой водой фракций фтора методом прямой потенциометрии с фторид-селективным электродом. Для анализа промышленной чёрной массы, содержащей смесь катодных материалов с преобладанием типа NCA ($LiNi_{1-x-y}Co_xAl_yO_2$), применяли водное и кислотное выщелачивание, а также прямое щелочное сплавление в смеси NaOH–KOH. Содержание водоэкстрагируемой фракции фтора составило (2,33 ± 0,06) мас.%. Вместе с тем кислотное выщелачивание и прямое щелочное сплавление исходной чёрной массы приводили к занижению определяемого содержания фтора, что указывало на матричное влияние алюминия на стадиях пробоподготовки. На модельном образце чистого ПВДФ показано, что щелочное сплавление обеспечивает эффективный перевод ковалентно связанного фтора в форму, доступную для потенциометрического определения. Установлено, что критическим фактором является переход Al в раствор с его последующим осаждением при корректировке pH, сопровождающимся частичным выведением фторида из определяемой растворённой формы. Водоэкстрагируемая фракция фтора может быть определена прямой потенциометрией с хорошей повторяемостью, тогда как количественная оценка неэкстрагируемой водой фракции после щелочного разложения существенно осложняется Al-индуцированной потерей фторида при нейтрализации. Выявленное влияние алюминия, присутствующего в реальной чёрной массе как в составе катодного материала, так и в виде металлических примесей, необходимо учитывать при разработке аналитических протоколов определения фтора в чёрной массе ЛИА.

Ключевые слова: литий-ионные аккумуляторы; чёрная масса; фтор; фторид-селективный электрод; прямая потенциометрия; щелочное сплавление; ПВДФ; $LiPF_6$; рециклинг.

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(2026) Chem Bull Kaz Nat Univ 4:N-NN

CHEMICAL BULLETIN
of Kazakh National University
http://bulletin.chemistry.kz/

IRSTI 31.19.15 https://doi.org/10.15328/cb2026_166

Article

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1. Introduction

Owing to their high specific energy density, elevated operating voltage, light weight, and compact design, lithium-ion batteries (LIBs) have become the preferred energy storage solution. Their widespread use in electric vehicles and portable electronics inevitably leads to the accumulation of spent batteries: assuming a service life of 10–15 years, the global electric vehicle fleet is expected to generate approximately 11 million tons of such waste by 2030 [1]. Spent LIBs contain flammable organic solvents, polymers, graphite, metal foils, transition metal oxides (Ni, Co, Mn, Fe), and lithium compounds, which pose environmental risks if disposed of improperly, while representing a valuable secondary source of critical metals when processed correctly [2]. From an economic standpoint, the most valuable fraction produced by the mechanical processing of spent LIBs is the black mass – a multicomponent mixture comprising anode graphite and cathode active material, in which the bulk of the valuable transition metals is concentrated, together with Al, Cu, and Fe impurities originating from the current collectors and cell casing components. In addition, the black mass retains residual electrolyte components and the polyvinylidene fluoride (PVDF) polymer binder, which are the principal sources of fluorine.

Among the constituents of black mass, fluorine-containing compounds occupy a special position: they are not target recycling products, yet they substantially complicate several processing stages, acting as corrosive and chemically aggressive components and affecting the chemistry of leaching [3]. The sources of fluorine in a battery are the cathode binder PVDF, the $LiPF_6$ salt of the electrolyte together with its hydrolysis and thermal decomposition products, and possible fluorine-containing electrolyte additives required for the stable formation of the solid electrolyte interphase (SEI) on the anode and the cathode electrolyte interphase (CEI) [4,5]. Expressed as elemental fluorine relative to the black mass, the fluorine content amounts to several weight percent (1–4 wt.%) [6]. $LiPF_6$ can decompose according to an equilibrium yielding LiF and PF_5, the latter being quantitatively hydrolyzed – even by trace amounts of water – to HF, POF_3, and fluorophosphates [5]:

$$LiPF_6 \leftrightarrow LiF + PF_5 \quad (1)$$

$$PF_5 + H_2O \rightarrow POF_3 + 2HF \quad (2)$$

$$POF_3 + H_2O \rightarrow HPO_2F_2 + HF \quad (3)$$

$$LiPF_6 + 4H_2O \rightarrow LiF + H_3PO_4 + 5HF \quad (4)$$

In aqueous solutions, fluoride corrodes process equipment, forms stable complexes with metal cations, and degrades the purity of the target products, in particular of the lithium salt (Li_2CO_3), whereas during pyrolysis the fluorine-containing components pass into the gas phase as HF, requiring dedicated off-gas treatment systems [7,8]. Alongside the mandatory recovery targets for Li, Co, Ni, and Cu set by Regulation (EU) 2023/1542 [9], the Chinese national standard GB/T 45203-2024 establishes a separate limit for water-soluble fluorine in recycled black mass of no more than 0.10–0.40 wt.% [10]. Meeting this requirement is impossible without dedicated defluorination stages.

The choice of defluorination stage is dictated by the form in which fluorine occurs in the material. During battery operation, storage, and preliminary processing, the original $LiPF_6$ electrolyte salt partially decomposes into various inorganic fluorine-containing compounds, including LiF and fluorophosphates [5]. Some of these compounds, along with

Received 05 Sep 2026; Received in revised form 22 Oct 2026; Accepted 28 Oct 2026; Available online 13 Nov 2026.

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adsorbed fluoride, can pass into the aqueous phase upon contact of the black mass with water and are treated in the present work as the water-extractable fluorine fraction. This fraction is removed by washing the black mass with water, after which fluoride can be removed from the resulting solutions by precipitation with aluminum sulfate at a pH of about 5 [11]. The residual, water-non-extractable fraction (hereafter the residual fraction) is associated primarily with PVDF, although it may also include sparingly soluble inorganic fluorides and electrolyte decomposition products. Fluorine covalently bound in PVDF behaves in a fundamentally different way: the polymer is resistant to acids and oxidants and remains in the solid residue under conventional leaching conditions [12]. Its removal requires either thermal treatment or alkaline degradation, in which PVDF undergoes dehydrofluorination with the formation of conjugated C=C bonds and the release of F^- [13]. Consequently, the same total fluorine content may call for different processing solutions depending on the ratio of the water-extractable and residual fractions, so determining the total fluorine content alone is not sufficient for selecting a defluorination scheme.

A wide range of analytical methods has been developed for fluorine determination, including ion chromatography, potentiometry with a fluoride-selective electrode, spectroscopic techniques, and titrimetric methods [14]. As applied to black mass, however, most existing approaches are aimed primarily at determining the total fluorine content and do not allow the water-extractable and residual fractions to be quantified separately [15,16].

Direct potentiometry with a fluoride-selective electrode (F-ISE) based on a LaF_3 single crystal is one of the most accessible methods for determining fluoride ion [17] and can be applied to the analysis of aqueous extracts of black mass. The electrode response is close to Nernstian over the working concentration range; correct determination, however, requires control of the ionic strength and pH of the solution, as well as masking of interfering polyvalent cations – those capable of forming weakly dissociated compounds with fluoride – by means of a total ionic strength adjustment buffer (TISAB) [18,19]. Complex formation is one of the principal sources of error in the potentiometric determination of fluoride, and citrate and other complexing agents are used to suppress this effect. The applicability of the F-ISE to LIB-related objects has previously been demonstrated for electrolyte systems: linear organic carbonates such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) do not significantly affect the electrode response, whereas in ion chromatographic determination the signals of matrix components may overlap [19]. In the analysis of real black mass, however, the presence of polyvalent metals becomes an additional factor. Aluminum is of particular importance, as it originates both from Al-containing cathode materials, notably $LiNi_{1-x-y}Co_xAl_yO_2$ (NCA), and from current collector fragments, and is capable of binding fluoride strongly [18,20]. Previous studies have addressed the interfering effect of aluminum in the measured solution, where Al–F complex formation can be suppressed by masking agents [20], and the deliberate use of aluminum sulfate for fluoride removal from NMC black mass leachates [11]. The behavior of aluminum contained in the black mass itself during analytical sample preparation has, however, received little attention, although the reliability of fluorine determination in black mass is governed not only by the performance characteristics of the F-ISE, but also by the retention of fluoride during the extraction, pH adjustment, and solution preparation stages.

The aim of the present work was to assess the feasibility of separately determining the water-extractable and residual fluorine fractions in the black mass of spent LIBs by direct potentiometry with an F-ISE, and to examine how different sample preparation schemes affect the results of the determination. To this end, water leaching, acid leaching, and alkaline fusion were compared, the conversion of PVDF-bound fluorine into a measurable ionic form was evaluated, and the effect of aluminum on fluoride retention during subsequent pH adjustment was investigated. Unlike the studies cited above, the present work concerns aluminum contained in the black mass itself, in the NCA cathode material and in current collector fragments, which causes fluoride loss at the neutralization stage, i.e., before the measurement, so that this error cannot be eliminated by TISAB. To the best of our knowledge, this is the first experimental demonstration that, in the analytical sample preparation of LIB black mass, the transfer of aluminum contained in the material into solution followed by its precipitation upon pH adjustment can lead to a substantial systematic underestimation of the measured fluorine content.

2. Experiment

2.1 Materials and reagents

The following reagents were used in this work: PVDF (battery grade, Sigma-Aldrich), sodium fluoride (NaF, Sigma-Aldrich), aluminum sulfate octadecahydrate ($Al_2(SO_4)_3 \cdot 18H_2O$, Reakhim, Russia), glacial acetic acid (CH_3COOH) and n-hexane (EKOS-1, Russia). Hydrogen peroxide (H_2O_2, 33 wt.%), nitric acid (HNO_3, 65 wt.%), hydrochloric acid (HCl, 37 wt.%), sulfuric acid (H_2SO_4, 96 wt.%), sodium hydroxide (NaOH, ≥99.9%), potassium hydroxide (KOH, ≥99.99%), sodium chloride (NaCl), trisodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), and sodium acetate trihydrate ($CH_3COONa \cdot 3H_2O$) were purchased from Labhimprom (Kazakhstan). All reagents were of analytical grade or higher and were used without further purification. Distilled water was used throughout.

The spent LIB black mass was supplied by Techno Destroy, a battery recycling company based in Almaty, Kazakhstan. The cathodic part of the provided LIB black mass is a mixture of $LiNi_xCo_yMn_zO_2$ (NCM) and NCA. The material was a fine black powder. Prior to use, the sample was homogenized in a planetary ball mill (BM6 Pro, ZrO_2 jars and balls, 400 rpm) in hexane for 2 h in order to average its chemical and phase composition and to break up agglomerates and was then dried at 80 °C under vacuum for 12 h to remove residual solvent and moisture.

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2.2 Analytical techniques and instrumentation

The contents of the major metals in the black mass under study were determined by atomic absorption spectroscopy (AAS). A 0.50 g portion of black mass was leached with aqua regia (15 cm^3, HCl:HNO_3= 3:1) at room temperature for 12 h; the solution was filtered (slow filter paper, pore size 2–3 μm), made up to 250 cm^3, and analyzed on an AA-6200 spectrometer (Shimadzu, Japan) in flame mode (air–acetylene flame) at the recommended analytical lines of the elements after appropriate dilution (×10, ×100). The experiments were carried out in five replicates, and the reported values are the corresponding means.

The phase composition of the black mass was studied by X-ray diffraction (XRD) on a TD-3700 diffractometer (Tongda, China) using Cu $K\alpha_1$ radiation (λ = 1.54056 Å) over the range 2θ = 5–80° with a step of 0.02°. Phase identification was performed in HighScore Plus using the PDF-2 database.

The surface morphology and local elemental composition of the black mass were examined by scanning electron microscopy with energy-dispersive X-ray microanalysis (SEM-EDS) on a SEM5000Pro microscope (CIQTEK, China) with an Oxford Instruments X-Plore 30 silicon drift detector (SDD); EDS spectra were acquired at an accelerating voltage of 20 kV.

2.3 Preparation of the total ionic strength adjustment buffer

The TISAB was prepared according to the composition given in the data sheet of the ELIS-131F fluoride-selective electrode used in this work [21]. To prepare the buffer, 58.0 g of NaCl, 3.0 g of trisodium citrate dihydrate, and 30.0 g of sodium acetate trihydrate were dissolved in approximately 500 cm^3 of distilled water, 57.0 cm^3 of glacial acetic acid was added, and the solution was made up to the mark with distilled water in a 1000 cm^3 volumetric flask. The pH of the prepared buffer was ~5.

2.4 Potentiometric measurements and calibration

Measurements were performed on an I-160MI ion meter with an electrode pair consisting of an ELIS-131F fluoride-selective electrode (membrane based on a LaF_3 single crystal) and a silver–silver chloride reference electrode, under continuous stirring with a magnetic stirrer at 20 °C. The steady-state potential was established within 1–3 min.

A 50 cm^3 aliquot of the sample solution was mixed with 50 cm^3 of TISAB, and the electrodes were immersed; the potential was recorded once it had stabilized. The pH was monitored before and after the addition of the buffer and in all cases amounted to ~4.9–5.0 after the introduction of TISAB. The pH of the solutions was controlled with the same I-160MI ion meter using an ESK-10603/7 combined glass pH electrode, calibrated beforehand against standard buffer solutions with pH 4.01, 6.86, and 9.18.

The fluoride-selective electrode was calibrated against F^- standard solutions with concentrations ranging from 10^{-1} to 10^{-5} mol/dm^3. A stock NaF solution of 10^{-1} mol/dm^3 was prepared from an accurately weighed portion of pre-dried NaF, and solutions of lower concentration were obtained by serial dilution. Before the potentiometric measurement, the standard solutions were mixed with TISAB in the same ratio as the samples, ensuring an identical background electrolyte composition during calibration and analysis.

2.5 Sample preparation for the determination of fluorine fractions

Several sample preparation schemes were used for the determination of fluorine in the black mass: water leaching to isolate the water-extractable fraction, acid leaching as an alternative means of matrix decomposition, and alkaline fusion to convert the residual fraction into a soluble form.

Water leaching. A portion of black mass of about 1 g (weighed to the nearest 0.0001 g) was placed in a beaker and distilled water was added at a solid-to-liquid ratio of S:L = 1:50 (g/cm^3). The suspension was stirred on a magnetic stirrer at room temperature for 12 h, after which the solid phase was separated by filtration through ashless filter paper (slow grade). The filter cake and the receiving flask were then washed 3–5 times with 10–15 cm^3 portions of distilled water, and the washings were combined with the filtrate. The combined solution was transferred quantitatively into a 500 cm^3 volumetric flask and made up to the mark with distilled water. The resulting solution was used for the potentiometric determination of the water-extractable fluorine fraction. The washed solid residue was dried to constant mass at 80 °C and used for the determination of the residual fraction by alkaline fusion.

Acid leaching. To assess the influence of acid decomposition of the matrix on the results of fluorine determination, a solution of 2 M H_2SO_4 with the addition of 5 vol% H_2O_2 was used, this being a common lixiviant in the hydrometallurgical processing of LIB black mass [22]. A portion of black mass of about 1 g was leached at S:L = 1:50 at room temperature for 12 h under stirring. After filtration, the filter cake and the receiving flask were washed 3–5 times with 10–15 cm^3 portions of distilled water, and the washings were combined with the leachate. The combined solution was neutralized to pH 6–7 by dropwise addition of concentrated NaOH solution under stirring and continuous pH control, transferred quantitatively into a 500 cm^3 volumetric flask, and made up to the mark with distilled water.

Alkaline fusion. To convert the water-non-extractable fluorine-containing components into a soluble form, a 0.50–0.55 g portion of black mass was placed in a glassy carbon crucible and a 1:1 mass ratio mixture of NaOH and KOH with a total mass of 6 or 8 g was added. The crucible was covered with a lid and placed in a muffle furnace (SNOL 10/1300 LSM01). Heating was carried out in two stages: to 300 °C at a rate of 5 °C/min with a 2 h hold, then to 480 °C at the same rate with a further 2 h hold. After cooling, the melt was dissolved in 100–150 cm^3 of hot distilled water and filtered; the residue on the filter was washed with hot distilled water, and the washings were combined with the filtrate. The filtrate was neutralized to pH 6–7 by dropwise addition of concentrated HCl (37%) under stirring and continuous pH control, transferred quantitatively into a 500 cm^3 volumetric flask, and made up to the mark with distilled water.

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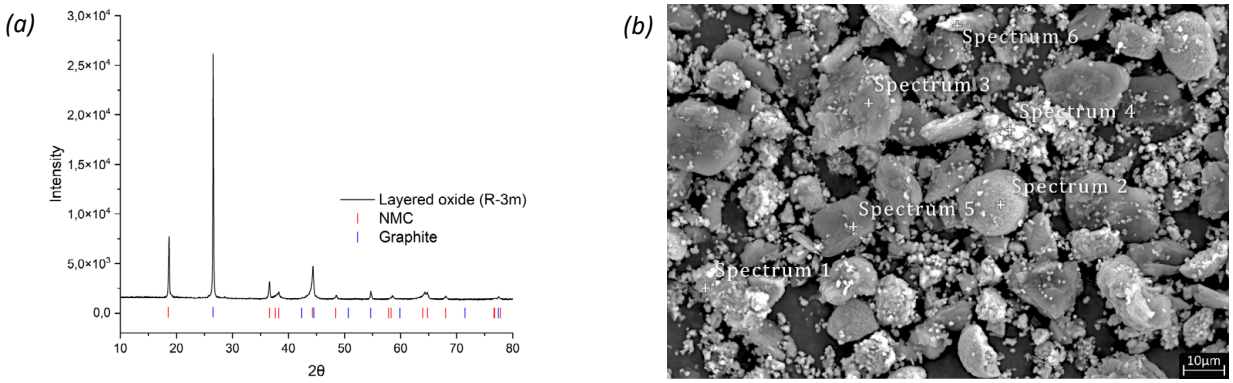


Figure 1 – (a) X-ray diffraction pattern and (b) SEM image of the black mass, showing the points of local EDS analysis

Commercial powdered PVDF was used as a model object to evaluate the completeness of conversion of PVDF-bound fluorine into a measurable ionic form. The theoretical fluorine mass fraction calculated for the repeating unit –[CH_2–CF_2]– (M = 64.03 g/mol) is 59.34%. PVDF portions of 0.085–0.104 g were subjected to alkaline fusion by the same procedure as the black mass samples; after dissolution of the melt and subsequent sample preparation, the solutions were transferred quantitatively into 250 cm^3 volumetric flasks and made up to the mark with distilled water.

2.6 Data processing and calculation of the F^- concentration

The dependence of the fluoride-selective electrode potential on the fluoride ion concentration was described by the linear equation (5):

$$E = a + b \cdot pF \quad (5)$$

where E is the measured potential of the electrode system, mV; a is the intercept, mV; b is the slope of the calibration dependence, mV/dec; and $pF = -\log C(F^-)$, where $C(F^-)$ is the molar concentration of fluoride ion. The linear regression parameters were determined by unweighted least squares.

The fluoride ion concentration in the sample solution was determined from the calibration dependence on the basis of the measured potential of the electrode system. Since the standard and sample solutions were mixed with TISAB in the same volume ratio (1:1) and the calibration dependence was constructed using the nominal concentrations of the standards before mixing with TISAB, the concentration obtained from equation (5) refers directly to the sample solution before the addition of TISAB, and no additional correction for dilution is required. The fluorine mass fraction ω(F) (equation 6) was calculated from the F^- concentration, the final solution volume, the molar mass of fluorine, and the mass of the initial sample portion:

$$\omega(\mathrm{F}) = \frac{\mathrm{C}(F^-) \cdot V \cdot M(F)}{m_0} \times 100\ \% \quad (6)$$

where $C(F^-)$ is the fluoride ion concentration, mol/dm^3; V is the volume of the volumetric flask, dm^3; M(F) = 18.998 g/mol; and m_0 is the mass of the sample portion, g.

The results are reported as $\bar{X} \pm \Delta$, where $\bar{X}$ is the arithmetic mean and $\Delta = t(P, f) \cdot s/\sqrt{n}$ is the half-width of the confidence interval at a confidence level P = 0.95 and $f = n - 1$ degrees of freedom (s is the standard deviation and n is the number of parallel determinations). Repeatability was characterized by s and the relative standard deviation (RSD). The equality of variances of two independent samples was checked using the F-test, and the statistical significance of differences between their means was assessed using the two-sided Welch t-test, which does not require the assumption of equal variances [23,24]. Differences were considered statistically significant at $p < 0.05$.

3. Results and Discussion

3.1 Characterization of the as-received black mass

Since industrial black mass may be heterogeneous with respect to the type of cathode component, the first step was to establish which cathode material predominates in the sample. Figure 1a shows the X-ray diffraction pattern of the as-received electrode mass. The observed reflections correspond to a layered structure of the α-$NaFeO_2$ type (space group R-3m) typical of $LiMO_2$ cathode materials; the peaks are indexed to the (003), (101), (006)/(012), (104), (015), (107), (018), (110), and (113) planes. A graphite reflection is also present at 2θ ≈ 26.5° (the (002) plane). Owing to the similarity of the lattice parameters within NCM systems, XRD does not allow the exact ratio of the transition metals to be determined unambiguously.

Local SEM-EDS analysis (Figure 1b) revealed a pronounced phase heterogeneity of the material. Spectra 1 and 4 were acquired on agglomerates of cathode particles with graphite, where fluorine (9.9–10.6 wt.%) was detected alongside Ni and Co in combination with phosphorus, consistent with the presence of fluorine-containing electrolyte residues and/or PVDF. Spectrum 2 corresponds to a particle of a high-nickel layered oxide of the NCA type (Ni 57.00, Co 6.33, Al 0.61 wt.%).

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Spectra 3 and 5 relate to anode graphite (C 95.7–99.1 wt.%), the presence of copper in spectrum 5 indicating the incorporation of current collector fragments during mechanical processing. Spectrum 6 corresponds to a manganese-containing phase (Mn 51.05 wt.%) attributable to a lithium–manganese oxide.

According to the AAS data, the total contents of the major metals in the black mass were (wt.%): Ni – 27.99; Co – 4.25; Mn – 0.36; Li – 2.97; Cu – 0.21; and Al – 0.62. The residue insoluble in aqua regia, determined gravimetrically, accounts for a substantial part of the black mass (≈39 wt.%). It consists predominantly of anode graphite but may also contain conductive carbon black, PVDF and other insoluble components; this value should therefore be regarded as an upper estimate of the graphite content. The presence of Al is due both to its incorporation into the NCA cathode material and to the possible introduction of aluminum current collector fragments during the mechanical processing of the batteries. The high nickel content combined with the low manganese fraction is consistent with the EDS data and corresponds to an industrial mixture of spent cathode materials in which NCA predominates, with minor manganese-containing inclusions.

3.2 Calibration characteristics of the fluoride-selective electrode

The calibration dependence of the F-ISE response was constructed using a series of NaF standard solutions prepared and measured with the addition of TISAB, which provides a constant ionic strength and pH of the medium. The potential was measured by direct potentiometry against a silver–silver chloride reference electrode (Figure 2).

The resulting dependence is described by equation (5) with the parameters a = (−562.49 ± 3.62) mV and b = (57.85 ± 1.09) mV/decade (five calibration points). The Pearson correlation coefficient was r = 0.9995 and the coefficient of determination R^2 = 0.9989, with a residual sum of squares of 35.71 mV^2, corresponding to a residual standard deviation of 3.45 mV. The experimental slope of (57.85 ± 1.09) mV/decade is close to the theoretical value of 58.16 mV/decade, indicating a near-Nernstian response of the electrode.

The lowest calibration standard of 10^{-5} mol/dm^3 corresponds, for a sample solution volume of 500 cm^3, and a sample portion of 1 g, to a fluorine mass fraction of about 0.0095 wt.% in the original sample. This value characterizes the lower boundary of the calibrated range and should not be regarded as the limit of quantification of the procedure, which was not determined in this work. All fluoride concentrations measured in the sample solutions (≥1.35·10^{-4} mol/dm^3) lay within the calibrated range and more than an order of magnitude above the lowest standard.

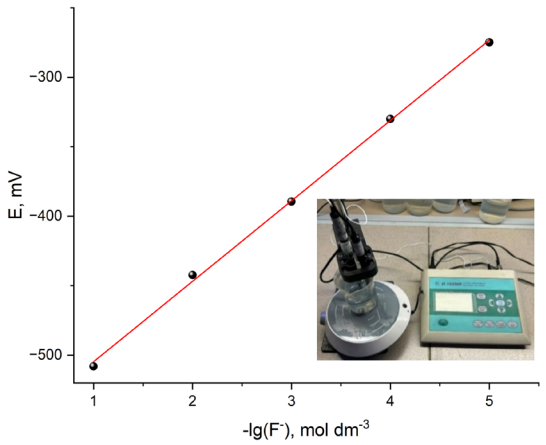


Figure 2 – Calibration dependence of the fluoride-selective electrode potential on −log C(F$^-$) for NaF standard solutions

3.3 Evaluation of alkaline fusion using a model PVDF sample

PVDF is one of the principal potential sources of the residual fluorine fraction in black mass. To assess the ability of the selected alkaline fusion procedure (Section 2.5) to convert fluorine covalently bound in PVDF into an ionic form accessible to F-ISE determination, portions of the commercial polymer were analyzed (Table 1).

The mean fluorine content found was (61.7 ± 0.7) wt.%, against a theoretical content of 59.3 wt.% calculated for the repeating unit –[CH_2–CF_2]–. The ratio of the found content to the theoretical value was 104.0%. The low RSD (0.43%) indicates good repeatability of the procedure. The found value exceeds the theoretical one by about 4%, which corresponds to a shift in the measured potential of only about 1 mV (57.85 mV/dec × log 1.04), well within the residual standard deviation of the calibration (3.45 mV). The deviation is therefore most likely attributable to the calibration uncertainty; a possible deviation of the actual composition of the commercial product from the

Table 1 – Results of fluorine determination in model PVDF samples after alkaline fusion

№	m_o, g	V, dm³	C(F⁻), mol/dm³	ω(F), wt.%
1	0.1036	0.25	1.34·10^{-2}	61.4
2	0.1037	0.25	1.35·10^{-2}	61.7
3	0.0854	0.25	1.11·10^{-2}	61.9
			Mean ± Δ (P = 0.95)	61.7 ± 0.7
			s	0.27
			RSD, %	0.43

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ideal homopolymer formula cannot be excluded either. Being positive, the deviation does not indicate fluorine losses during the alkaline fusion of pure PVDF.

3.4 Content of the water-extractable fluorine fraction in the black mass

The content of the water-extractable fluorine fraction was determined after 12 h of leaching of the black mass with distilled water at S:L = 1:50. The fluorine mass fraction was calculated relative to the mass of the initial black mass portion (Table 2).

The content of the water-extractable fluorine fraction in the black mass under study was (2.33 ± 0.06) wt.% (n = 5, RSD = 2.17%). The low RSD indicates good repeatability of the water extraction procedure and of the subsequent potentiometric determination. The content found substantially exceeds the limits for water-extractable fluorine set by GB/T 45203-2024 for the various categories of recycled black mass (0.10–0.40 wt.%). At S:L = 1:50, the fluorine content found corresponds to a concentration of about 0.47 g/dm³ in the aqueous extract prior to subsequent dilution. Even on the tentative assumption that all of the extractable fluorine is present as LiF, this corresponds to approximately 0.64 g/dm³ LiF, which is below its solubility in water (~1.3 g/dm³) [25]. The selected S:L ratio therefore imposes no limitation associated with saturation of the solution with respect to LiF and, if LiF predominates among the water-extractable fluorine species, is sufficient in terms of solubility for their transfer into the aqueous phase.

Expressed tentatively in terms of individual compounds, the amount of water-extractable fluorine found corresponds to 3.10 wt.% $LiPF_6$ or 3.17 wt.% LiF relative to the initial black mass, which is consistent with the average residual electrolyte content reported for black mass that has not been subjected to water washing [26].

3.5 Effect of acid leaching on the results of fluorine determination

Acid leaching is widely used in the hydrometallurgical processing of black mass [27] and is accompanied by dissolution of a substantial part of the cathode material and of a number of metallic components of the mixture. To assess the influence of such sample preparation on the results of potentiometric fluorine determination, the black mass was leached with a well-established solution of 2 M H_2SO_4 containing 5 vol.% H_2O_2 [22].

The mean fluorine content determined after acid leaching and subsequent neutralization of the solution was (1.33 ± 0.07) wt.% (n = 7, RSD = 5.60%), which is statistically significantly lower than the content of the water-extractable fluorine fraction, (2.33 ± 0.06) wt.% (t = 27.6, $p < 0.001$; the variances did not differ significantly, F = 2.18, p = 0.47). Since acid decomposition involves a deeper destruction of both the cathode matrix and the other components of the black mass, the observed decrease in the analytical signal points to losses or binding of fluoride at the sample preparation stages.

One possible cause initially considered was the formation of stable Al–F complexes with aluminum passing into solution during acid leaching. The effect of Al^{3+} on the potentiometric determination of fluoride is well known and is associated with the high stability of its fluoride complexes [18,20]. In an additional experiment, however, the addition of citrate in excess of the amount introduced with the TISAB did not increase the measured F^- concentration. Furthermore, when a fluoride standard addition (standard addition method, $C(F^-) = 1.00 \cdot 10^{-2}$ mol/dm³) was introduced directly into the prepared acid leachate – that is, after filtration and after the stages at which fluorine loss is presumed to occur – the recovery of the added F^- was 100.1%. These results show that no significant masking of F^- by components of the black mass takes place in the solution delivered directly to the potentiometric measurement. The decrease in the fluorine content therefore arises before the measurement stage.

The most probable stage of fluoride loss is the neutralization of the acid leachate. After leaching, aluminum is predominantly in dissolved form. Upon the subsequent increase of pH with NaOH solution to 6–7, required for the further preparation of the solution for potentiometric measurement, Al(III) undergoes hydrolysis with the formation of hydroxide, oxyhydroxide, and hydroxysulfate phases. Intensive precipitation of Al-containing compounds occurs in the pH range 4–6, through which the solution inevitably passes during

Table 2 – Determination of the water-extractable fluorine fraction in the black mass

№	m_o, g	$C(F^-)$, mol/dm³	ω(F), wt.%
1	1.0019	$2.52 \cdot 10^{-3}$	2.39
2	1.0089	$2.43 \cdot 10^{-3}$	2.28
3	1.0295	$2.56 \cdot 10^{-3}$	2.37
4	1.0189	$2.46 \cdot 10^{-3}$	2.29
5	1.0364	$2.50 \cdot 10^{-3}$	2.30
		Mean ± Δ (P = 0.95)	2.33 ± 0.06
		s	0.050
		RSD, %	2.17

Table 3 – Results of fluorine determination after acid leaching of the black mass

№	m_o, g	$C(F^-)$, mol/dm³	ω(F), wt.%
1	1.0134	$1.39 \cdot 10^{-3}$	1.30
2	1.0065	$1.42 \cdot 10^{-3}$	1.34
3	1.0153	$1.51 \cdot 10^{-3}$	1.41
4	1.0227	$1.33 \cdot 10^{-3}$	1.24
5	1.1085	$1.46 \cdot 10^{-3}$	1.25
6	1.0080	$1.52 \cdot 10^{-3}$	1.43
7	1.0073	$1.42 \cdot 10^{-3}$	1.34
		Mean ± Δ (P = 0.95)	1.33 ± 0.07
		s	0.074
		RSD, %	5.60

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neutralization. In this same range, and particularly at a pH of about 5, efficient binding of fluoride by aluminum-containing precipitates is observed [11]. Accordingly, the neutralization step that precedes the potentiometric determination simultaneously creates the conditions for the removal of part of the fluoride from the dissolved form. No macroscopic precipitate was observed visually; therefore, the nature and physical state of the Al-containing species were not directly characterized.

The acid leaching scheme with subsequent neutralization used here is thus unsuitable for the correct potentiometric determination of fluorine without additional control or prior separation of aluminum. Water leaching is more reliable for the determination of the water-extractable fluorine fraction, since Al and Fe remain predominantly in the solid phase.

3.6 Effect of direct alkaline fusion of the initial black mass on fluorine determination

For an additional check on the consistency of the results obtained, the as-received black mass was subjected to alkaline fusion directly, without prior water leaching. It was expected that under fusion conditions the fluorine of the residual fraction, including PVDF-bound fluorine and other sparingly soluble fluorine-containing components, would be converted predominantly into soluble Na and K fluorides. After dissolution of the melt in water, both the products of the alkaline conversion of the residual fraction and the originally water-extractable fluorine should pass into the solution to be analyzed. The results obtained with different masses of the NaOH–KOH mixture are given in Table 4.

Table 4 – Results of fluorine determination after direct alkaline fusion of the as-received black mass.

Mass of NaOH:KOH = 1:1 mixture	n	ω(F) ± Δ (P = 0.95), wt.%	s, wt.%	RSD, %
6 g	5	2.16 ± 0.18	0.15	6.81
8 g	8	2.20 ± 0.17	0.21	9.41
All series	13	2.19 ± 0.11	0.18	8.25

The mean fluorine content determined after direct alkaline fusion was (2.19 ± 0.11) wt.% (n = 13, RSD = 8.25%). This value was statistically significantly lower than the content of the water-extractable fluorine fraction, (2.33 ± 0.06) wt.% (Welch t-test: t = 2.48, p = 0.025; the variances differed significantly, F = 12.9, p = 0.025), even though direct fusion of the as-received black mass was expected to bring the residual, water-non-extractable fluorine additionally into soluble form. The absence of the expected increase in the measured fluorine content indicates its partial loss from the dissolved form during the subsequent sample preparation. Under alkaline fusion, the aluminum contained in the black mass is converted predominantly into soluble aluminate species, while the residual fluorine, including that bound in PVDF, is converted mainly into soluble Na and K fluorides. Upon dissolution of the melt, aluminum remains predominantly in the soluble aluminate form, nominally $Al(OH)_4^-$; however, upon the subsequent acidification with HCl to pH 6–7, the stability of the aluminate species decreases and sparingly soluble hydroxide and oxyhydroxide Al phases are formed. Their precipitation in the presence of fluoride can presumably lead to its sorption, co-precipitation, and/or incorporation into Al–F-containing phases. As a result, part of the fluorine is apparently removed from the dissolved form and becomes inaccessible to the subsequent F-ISE determination.

A comparison of the three sample preparation schemes studied shows that the determining factor is not the direction of the pH change as such, but the transfer of aluminum into solution – from the metallic form or from the NCA phase followed by its precipitation. Under water leaching, aluminum remains predominantly in the solid phase, and no pronounced decrease in the measured water-extractable fluorine content is therefore observed. Under acid leaching, Al passes into solution in cationic form and precipitates upon the subsequent increase in pH, whereas under alkaline fusion it is present predominantly as aluminate and forms sparingly soluble hydroxide and oxyhydroxide phases upon acidification of the melt solution to pH 6–7. In both cases, the precipitation of Al-containing phases occurs in the presence of fluoride and is most probably accompanied by its partial removal from the dissolved form through sorption, co-precipitation, and/or incorporation into Al–F-containing compounds. As a result, the fluorine content measured by F-ISE is systematically underestimated. The critical stage of the sample preparation schemes studied is therefore most probably associated with the precipitation of aluminum after its prior transfer into solution, rather than the acidic or alkaline nature of the medium as such.

3.7 Residual fluorine fraction and the role of aluminum

To evaluate the fluorine content remaining in the solid phase after water leaching, the entire dried residue obtained from a known portion of the as-received black mass was subjected to alkaline fusion. The fluorine mass fraction was calculated relative to the mass of the initial black mass. The results are presented in Table 5.

The content of the residual, water-non-extractable fluorine fraction determined after alkaline fusion was (0.229 ± 0.027) wt.% (*n* = 5, RSD = 9.5%). This value is substantially lower than the content of the water-extractable fraction, (2.33 ± 0.06) wt.%. It cannot, however, be regarded as a quantitative estimate of the true residual fluorine content, since, as shown above, the alkaline fusion scheme with subsequent neutralization of the melt solution leads to underestimated results. At the same time, the low content found is not due to an inability of the alkaline melt to decompose PVDF. For the model sample of pure PVDF, the ratio of the fluorine content found to the theoretical value was 104.0%, which demonstrates the efficient conversion of PVDF-bound fluorine into a form accessible to potentiometric determination. The fundamental difference in the case of real

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Table 5 – Results of the determination of the residual, water-non-extractable fluorine fraction in the solid residue after water leaching of the black mass by alkaline fusion

№	m_o, g	m_{flux}, g	E, mV	pF	C(F^-), mol/dm³	m(F), mg	ω(F), wt.%
1	1.0638	12.7502	−352.8	3.625	$2.37 \cdot 10^{-4}$	2.25	0.212
2	1.0999	13.1203	−359.2	3.514	$3.06 \cdot 10^{-4}$	2.91	0.264
3	1.0356	12.4221	−354.4	3.597	$2.53 \cdot 10^{-4}$	2.40	0.232
4	1.0337	12.4144	−354.0	3.604	$2.49 \cdot 10^{-4}$	2.37	0.229
5	1.0190	12.2829	−351.5	3.647	$2.25 \cdot 10^{-4}$	2.14	0.210
						Mean ± Δ (P = 0.95)	0.229 ± 0.027
						s	0.022
						RSD, %	9.5

black mass is the presence of aluminum and other matrix components, which also pass into solution during alkaline fusion.

For a direct experimental verification of the role of aluminum in the occurrence of fluorine losses, 1.00 mmol of Al as $Al_2(SO_4)_3$ was additionally introduced into the acid leachate before the neutralization step, after which neutralization and potentiometric determination were carried out according to the standard procedure (Table 6).

Following the introduction of Al, the measured fluorine content decreased from (1.33 ± 0.07) to (0.134 ± 0.032) wt.%, i.e., by approximately 90%. Since aluminum was introduced immediately before neutralization while all other stages of the analysis remained unchanged, this experiment shows that the presence of Al during pH adjustment strongly decreases the measured fluoride content. By analogy with the literature data [11], the most probable mechanism is sorption and/or co-precipitation of fluoride with Al-containing hydroxide phases, although the composition of these phases was not characterized in this work.

Taken together, the results indicate that the systematic underestimation is not related to the performance of the fluoride-selective electrode but is associated with the presence of dissolved aluminum during pH adjustment. Under water leaching, Al is expected to remain predominantly in the solid phase, whereas under acid leaching and alkaline fusion it passes into solution and, upon neutralization, presumably forms sparingly soluble Al-containing phases that remove part of the fluoride from the measurable dissolved form. Incomplete decomposition of PVDF in the real black mass matrix cannot be completely excluded as an additional factor. The value of (0.229 ± 0.027) wt.% obtained for the residue after water leaching should therefore be regarded as the fluorine content found experimentally by the procedure used, rather than as a quantitatively established true content of the residual fraction.

Table 6 – Effect of the additional introduction of aluminum before neutralization of the acid leachate on the results of fluorine determination

№	m_o, g	C(F^-), mol/dm³	ω(F), wt.%
1	1.0578	$1.42 \cdot 10^{-4}$	0.127
2	1.0206	$1.35 \cdot 10^{-4}$	0.126
3	1.0405	$1.64 \cdot 10^{-4}$	0.150
		Mean ± Δ (P = 0.95)	0.134 ± 0.032
		s	0.013
		RSD, %	9.80

4. Conclusions

The feasibility of separately determining the water-extractable and residual fluorine fractions in the black mass of spent LIBs by direct potentiometry with an F-ISE was evaluated. Water leaching provides reproducible determination of the water-extractable fraction, which in the studied sample was (2.33 ± 0.06) wt.%; since the F-ISE responds only to free F^-, this value refers to water-extractable fluoride. It considerably exceeds the regulatory limits for recycled black mass (0.10–0.40 wt.%), confirming the need for a defluorination stage in industrial processing.

Acid leaching and direct alkaline fusion with NaOH–KOH followed by neutralization to pH 6–7 underestimate the measured fluorine content relative to the aqueous extract (1.33 and 2.19 wt.%, respectively), which does not correspond to the expected total content. At the same time, alkaline fusion of pure PVDF efficiently converts covalently bound fluorine into an ionic form, showing that the fusion procedure itself is suitable for decomposition of the binder; incomplete decomposition of PVDF in the real black mass matrix, however, cannot be completely excluded.

It was established experimentally that the introduction of Al before neutralization decreases the measured fluorine content by about 90%. Excess citrate and a standard addition to the final solution (100.1% recovery) exclude masking of F^- in the

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measured solution, so the losses occur before the measurement stage. Aluminum, a constituent of the NCA cathode material that is also present as metallic impurities, dissolves under acidic or alkaline decomposition; the most probable mechanism of fluoride loss is its sorption and/or co-precipitation with sparingly soluble Al-containing phases formed upon pH adjustment. Reliable determination of the total and residual fluorine in LIB black mass therefore requires either separation of aluminum or verification of analyte recovery.

Acknowledgments

This work was carried out with the financial support of the Ministry of Science and Higher Education of the Republic of Kazakhstan (grant No. BR27198753).

Conflict of interest

The authors declare no conflict of interest.

CRediT authorship contribution statement

S. Malik: Conceptualization, Methodology, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. A. Tanash: Investigation, Validation, Writing – original draft. S. Uskov: Investigation, Validation, Visualization. A. Tazhibayeva: Investigation, Validation, Writing – review & editing. T. Kan: Investigation, Validation, Writing – review & editing. F. Malchik: Conceptualization, Supervision, Project administration, Funding acquisition, Writing – review & editing.

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