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Determination of the total fluorine content and quantification of the PVdF binder amount in lithium ion battery materials by combustion ion chromatography

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ABSTRACT

Lithium ion batteries (LIBs) typically contain fluorinated compounds, such as the inorganic conducting electrolyte salt ($LiPF_6$) or organic electrode binders like polyvinylidene fluoride (PVdF). While combustion ion chromatography (CIC) enables reliable quantification of the total fluorine content, it cannot differentiate between inorganic and organic fluorine compounds, thereby not allowing the selective determination of (organic) PVdF content. This study focused on identifying the most suitable calibration strategy for the quantification of PVdF. Calibration approaches based on inorganic fluorine standards, pure PVdF, and matrix-matched electrodes were systematically evaluated. Particular attention was given to complex sample matrices, such as black mass from recycling, which contain additional fluorine-containing compounds contributing to the overall fluorine signal. The influence of these species on PVdF quantification, as well as the feasibility of their selective removal, was investigated. Application to black mass samples revealed that calibration with pure PVdF allowed rapid estimation but introduced systematic deviations due to matrix effects. In contrast, matrix-matched calibration improved trueness and enabled PVdF quantification down to a limit of quantification (LOQ) of 1.39 µg PVdF. These findings highlight the importance of appropriate calibration and sample preparation strategies when applying the CIC technique to recycled materials.

1. Introduction

The growing demand for portable consumer electronics, electric vehicles and stationary energy storage systems has led to a substantial increase in the use of lithium ion batteries (LIBs) [1]. The high energy density and decreasing cost of LIBs has resulted in their widespread usage as an alternative to other battery technologies [2]. Consequently, the number of spent LIBs and the overall production output are expected to rise considerably in the coming years. Therefore, the recycling of LIBs is of great environmental and economic importance [3,4]. It represents a key component of sustainable energy systems by enabling the recovery of critical and valuable materials such as lithium, nickel, and cobalt [5,6]. One major concern during recycling is the potential release of fluorine-containing compounds into the environment [7]. State-of-the-art LIBs contain a variety of fluorinated compounds, most notably the conducting electrolyte salt lithium hexafluorophosphate ($LiPF_6$) and the binder polyvinylidene fluoride (PVdF). As a fluoropolymer, PVdF belongs to the broader class of per- and polyfluoroalkyl substances (PFAS) and is consequently included in current PFAS restriction proposals [8,9]. In contrast, $LiPF_6$ is an inorganic fluoride salt that readily undergoes hydrolysis to release toxic HF and PF_5, posing additional environmental and safety concerns during recycling [10]. The release or transformation of both classes of fluorinated compounds during the recycling process can thus present distinct but equally significant challenges [8,11,12]. Furthermore, residual fluorine-containing compounds may interfere with downstream recycling processing steps, such as flotation [13,14]. In addition, the effective pre-separation is important for the quality of metal extraction in further cathode recycling steps [11]. However, fluorine-containing compounds are crucial for enhancing LIB performance by improving electrode stability and ionic conductivity, and facilitate the formation of an effective solid-electrolyte interphase (SEI), which is essential for battery

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longevity and safety [15–17].

The removal of the electrolyte, including the conducting salt, and of the electrode binder, can be achieved using various techniques. LIB electrolytes typically consist of lithium salts, predominantly fluorinated species, dissolved in organic solvents. While the lithium salts may be toxic, the organic solvents are generally volatile and flammable. Therefore, electrolyte removal requires special handling and treatment, while both salts and solvents are valuable for recovery. Common removal methods include pyrolysis, solvent extraction, and sub-/supercritical carbon dioxide extraction [18–20]. For the removal of fluorinated binders, industrial processes typically rely on physical crushing and heat treatment. In contrast, laboratory-scale approaches often employ solvent-based dissolution (*e.g.*, using N-methyl-2-pyrrolidone, NMP) or supercritical fluid extraction to achieve selective binder removal [11,21].

Combustion ion chromatography (CIC) represents a promising analytical technique for the quantification of the total fluorine content in solid battery materials. In principle, a CIC system consists of a combustion unit coupled to an ion chromatography (IC) system via an absorption unit. During the process, the sample is combusted in a high-temperature furnace. Continuous water addition shifts the equilibrium toward the formation of hydrogen halides and sulfur dioxide/sulfur trioxide from sulfur-containing species. The combustion gases are subsequently absorbed in an absorption solution, where the corresponding anions are formed. This solution is then injected into the IC and quantified using a conductivity detector [22]. CIC is already well established in the field of environmental analysis, for instance, in monitoring fluorine-containing pollutants in wastewater or sludge [23]. It is also applied in polymer production to assess the migration of PFAS from food contact materials into food, and thereby the potential exposure to humans [24]. In the context of LIBs, however, the method has not yet been implemented to the best of current knowledge. To date, the reliable quantification of fluoride in liquid samples has been accomplished using ion-exchange chromatography coupled with conductivity detection (IEC–CD) [25]. Accurate quantification of PVdF binder and residual conductive salts in solid materials (*e.g.*, black mass or electrodes) is essential for designing, integrating, and monitoring recycling procedures. CIC represents a relatively clean and efficient approach, generating minimal hazardous waste [26].

In addition to CIC, thermogravimetric analysis (TGA) is commonly employed to evaluate binder removal in bulk battery materials. In such measurements, the sample is subjected to controlled heating under inert or oxidative conditions, allowing the thermal decomposition of PVdF to be monitored *via* characteristic mass losses within defined temperature ranges [27,28]. While TGA can provide quantitative information on PVdF content, its accuracy is often limited in complex samples. Black mass, in particular, consists of a heterogeneous mixture of active materials at different states of aging, with binders, carbon additives, and electrolyte or SEI residues. As a result, overlapping decomposition processes can occur, masking the distinct mass loss associated with PVdF and complicating its reliable quantification, especially at low concentrations. Spectroscopic methods, including Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy, have been demonstrated to be effective in the detection of fluorine-containing battery components. These methods employ the identification of characteristic functional group vibrations, such as -CF_2 stretching modes associated with PVdF binder residues and P-F vibrations characteristic of $LiPF_6$ electrolyte salt, to facilitate the identification of fluorinated compounds on surfaces. However, these methods are incapable of quantifying the total bulk fluorine [29,30].

In this study, different calibration strategies were systematically evaluated for the quantification of PVdF in LIB materials using CIC. In particular, inorganic fluorine standards, pure PVdF, and matrix-matched electrodes were compared with respect to trueness, repeatability and applicability. Special emphasis was placed on the assessment of matrix effects, and the presence of other fluorine-containing compounds which can influence the quantification of PVdF in heterogeneous materials such as black mass.

2. Experimental Part

2.1. Materials

PVdF was obtained from Solvay (BEL) with a molecular weight (Mw) of 650 kg mol^{-1} and a dispersity of 1.9. Lithium iron phosphate (LFP) was purchased from IBU-tec (DE), carbon black (Super C65) was purchased from Imerys Graphite & Carbon (CHE) and lithium nickel manganese cobalt oxide (NMC622) was obtained from BASF (DE).

An aged negative electrode was obtained from a LiFUN Technologies Ltd. (200 mAh, LFP II AG, CHN) cell. The cell was opened inside an argon-filled glovebox, and the negative electrode was carefully separated from the positive electrode, including the separator and pouch foil. The electrode was divided into three portions: one remained untreated (**Anode-unwashed**), one was rinsed with dimethyl carbonate (DMC) to remove residual electrolyte and soluble SEI components (**Anode-washed**), and a third portion was first rinsed with DMC and subsequently washed with 0.5 M H_2SO_4 (**Anode-washed, H_2SO_4**) prior to further analysis. The same washing procedure was additionally carried out with pure PVdF.

For the analysis a commercially available shredded LIB recycling material, so-called black mass (**BM D1**), was used. This black mass served as a model material, with both untreated BM D1 and treated BM D1 (denoted as **BM D1 MeOH**, **BM D1 DMC**, **BM D1 DMC/H_2SO_4**) considered. Inductively coupled plasma optical emission spectroscopy (ICP-OES) results showed an elemental composition of the black mass of $Li_{0.87}Ni_{0.7}Mn_{0.15}Co_{0.15}O_2$. The analysis of the electrolyte detected: ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), and the degradation products ethylene glycol (EtGly), 2,5-dioxahexanedioicacid dimethyl ester (DMDOHC) and 2,5-dioxahexanedioicacid diethyl ester (DEDOHC). PF_6^- was detected as the anion of the conducting salt. Details on the data and applied processing and treatment procedures are provided in the two studies from Hesper et al. [31,32].

Samples of **NMC-Ref.** (3 wt% PVdF) were obtained from an in-house production line and used to validate the method in more complex matrices.

2.2. Preparation of Standards

$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) positive electrodes were used as matrix-matched standards for the external calibration of the CIC method. An electrode was prepared with a 3 wt% PVdF content for this purpose. To prepare the cathode paste, 3 wt% of PVdF (Solef 5130) was stirred in N-methyl-2-pyrrolidone (NMP, anhydrous, 99.5 %, Sigma-Aldrich, USA) overnight. Subsequently, 1 wt% carbon black (Super C65) was added as a conductive agent, along with 96 wt% of NMC622 as the active material to achieve a solid content of 55 wt%. The resulting electrode paste was homogenized using a high-energy disperser (Dissolver Dispermat LC30, VMA-Getzmann GmbH, DE) at 2500 rpm for 15 min, followed by 10 000 rpm for 45 min. The dispersion was transferred into a Teflon petri dish, dried overnight at 80 °C, and subsequently ground in a mortar to obtain a fine and homogeneous powder.

2.3. Combustion Ion Chromatography

The schematic setup of the combustion ion chromatography system is shown in Fig. 1. All measurements were performed in triplicate. Measurements were carried out using a combustion unit NSX-5000 from a1-environsciences equipped with a horizontal furnace (HF-500). Prior to analysis, ceramic boats were pre-baked to remove any potential impurities. The instrument utilized an Ar gas flow of 200 mL min^{-1} and O_2 gas flow of 400 mL min^{-1} as well as 100 mL min^{-1} Ar gas flow for the

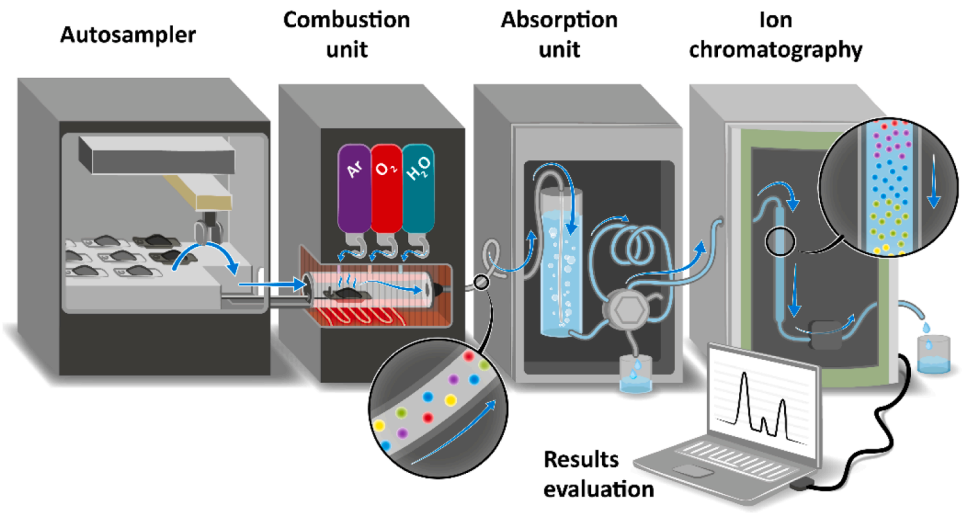

Fig. 1. Setup of the combustion ion chromatography system.

Table 1
Parameters set for IC–CD measurement.

IC - Parameter	Settings
Eluent	1 mM $NaHCO_3$ / 3.2 mM Na_2CO_3
Injection volume	100 µL
Flow rate	0.7 mL min^{-1}
Pressure	15 MPa
Temperature	30 °C
Detection	Conductivity

Milli-Q water throughput. The temperature of the combustion unit was 900 °C at the inlet and 1000 °C at the outlet. The gases were then absorbed in a GA-500 gas absorber unit using Milli-Q water, since this study focused only on determining fluorine, Milli-Q water was chosen as the absorption solution to minimize contamination from additional chemicals. The 10 ppm Bromide Standard (Sigma-Aldrich, USA) was added in the absorption solution as internal standard. The absorbed solution was injected, with an injection volume of 100 µL, into an 850 Professional IC Anion-MCS system (Metrohm, CHE). This was equipped with a Metrosep A Supp 5 (150 mm x 4 mm), 5 µm; Metrohm) used for isocratic anion separation. The flow rate of the IC–CD was set to 0.7 mL min^{-1} to ensure short analysis time and is at the upper end recommended by the column manufacturer. The chosen column is especially suitable for the separation of halogens. All measurements were carried out at moderate temperatures of 30 °C. The column material consists of a polyvinyl alcohol with quaternary ammonium modification. The parameters set for this separation technique are shown in Table 1. After injection into the ion chromatograph, the absorption tube was washed automatically with purified water.

3. Results and Discussion

Calibration strategies based on both inorganic fluorine solutions and solid organofluorine compounds were investigated for CIC, along with the influence of matrix components. In addition, black mass samples and selected fluorine-containing compounds (*e.g.*, $LiPF_6$ and LiF) were analyzed.

3.1. Calibration Strategy for PVdF Quantification by Combustion Ion Chromatography

First, different calibration strategies for the quantification of PVdF by CIC were systematically evaluated.

Calibration with inorganic fluorine solution

Calibration was performed using direct injection of an inorganic fluorine solution, omitting the combustion step. A five-point calibration with three replicated per point was prepared over a concentration range of 0.4–15 ppm F^-. Each calibration level yielded high repeatability with relative standard deviations (RSDs) ranging from 0.4 to 3.1 %. Retention times remained stable throughout the measurement series. Representative chromatograms and the corresponding calibration curve are provided in Fig. S1, Supporting Information.

The corresponding correlation coefficient (R^2), as well as limits of quantification (LOQ) were determined from linear regression analysis. LOQs were calculated based on the standard error of the y-intercept (σ_b) and the slope (m) of the calibration curve, using the formula LOQ = 10 σ_b/m. Calibration with an inorganic fluoride solution yielded a high correlation coefficient of 0.999. F^- had a LOQ of 0.36 ppm which corresponds to 16.34 µg PVdF under the applied sample preparation conditions.

The calibration of total fluorine analysis systems using inorganic fluorine standards assumes complete (100 %) combustion efficiency for solid (inorganic and organic) fluorine species. However, omitting specific steps in the analytical workflow, such as the direct injection of calibration standards into the IC, may increase the likelihood of overlooking potential sources of systematic error. Using a solid fluorine compound as a calibration standard incorporates the combustion step, thereby accounting for incomplete combustion efficiency. However, this approach is considerably more time-consuming [26]. Calibration with an inorganic fluorine solution, excluding the combustion step, was evaluated by assessing deviations between measured and theoretical fluorine contents in PVdF samples, see Fig. 2.

The combustion recovery rates, defined as the ratio of measured to prepared fluorine mass ($m_{measured}/m_{prepared}$), ranged between 85 % and 90 % across the investigated range of sample amounts with RSDs of 1.2–4.5 %, indicating good repeatability but a consistent underestimation of the theoretical fluorine content. These results are in line with reported variations in combustion efficiencies for PFAS compounds [26]. One possible explanation is the reaction of parts of the hydrogen fluoride, generated by the combustion of PVdF, with the silica tube in the furnace [33]. A more likely explanation, as already mentioned above, is that calibration based on aqueous IC standards does not account for the preceding combustion and absorption steps and therefore does not represent the entire analytical process. As a result, incomplete conversion or recovery of fluorine during the thermal decomposition of PVdF can lead to a systematic underestimation of the fluorine content [26].

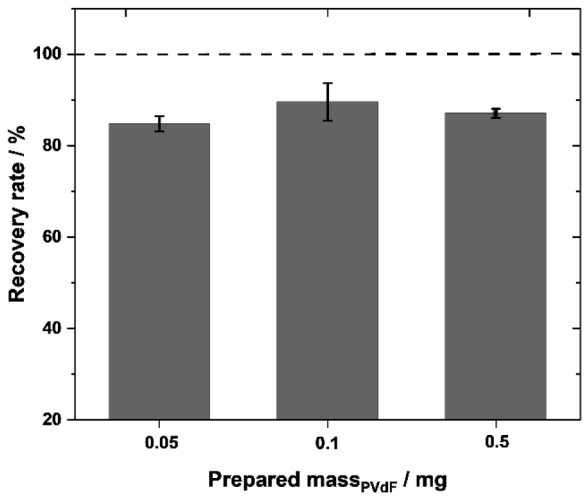

Fig. 2. Combustion recovery rate of PVdF based on calibration with inorganic fluorine solution.

Calibration was performed by direct injection of an inorganic fluorine solution, omitting the combustion step for simplicity and speed. This approach worked reasonably well for PVdF quantification but neglected potential losses during combustion, leading to reduced recovery.

Calibration with organic fluorine compound

To include the combustion and absorption process, multipoint calibration curves were established by combusting pure PVdF and PVdF dissolved in NMP, see Fig. 3. For the pure PVdF, the calibration curve was linear over the concentration range of 0.1–0.5 mg of PVdF, which corresponds to 2.4–11 ppm of F^-. The lower end of the calibration curve was limited by the weighing accuracy of the analytical balance. To circumvent the limitations of the analytical balance, a solution of PVdF and NMP was used and pipetted into the ceramic boats.

The ion chromatograms for the corresponding calibration for both, pure PVdF and PVdF in NMP solution, exhibited a consistent retention time of approximately 5.0 min and can be found in Fig. S2, Supporting Information. The resulting regression (R^2 = 0.999) for pure PVdF demonstrated excellent linearity within the investigated concentration range. The LOQ was 1.06 ppm F^-, corresponding to 48.17 µg PVdF, with RSDs of 1.4–10.0 %, indicating acceptable repeatability for quantitative fluorine determination.

However, samples such as black mass or process-control samples from delaminated active materials typically contain lower fluorine concentrations. Therefore, to ensure reliable quantification under realistic sample conditions, further optimization or extension of the calibration toward these lower concentration ranges was necessary.

For PVdF dissolved in NMP, the regression (R^2 = 0.997) demonstrated linearity within the investigated concentration range. In this case, the LOQ was lower at 0.16 ppm F^-, corresponding to 7.27 µg PVdF, and slightly lower repeatability with RSDs of 0.9–17.8 % were observed in comparison to the pure PVdF.

Although the strategy required an additional step of dissolving the PVdF in NMP, the total time required for both calibration approaches was comparable. A particular advantage of this approach was the use of a solution-based PVdF standard. This enabled more precise fluorine dosing via volumetric pipetting, which was especially beneficial at low analyte levels.

3.2. Matrix Effects in Combustion Ion Chromatography

The impact of matrix elements on the combustion behavior was investigated with LFP, NMC622 and carbon black composites containing PVdF at varying matrix-to-PVdF ratios. The PVdF recovery rate, calculated based on the PVdF calibration, was determined and is presented in Fig. 4.

The figures showed the recovery rate of PVdF, expressed as the ratio of measured to initially prepared mass. The pure matrix materials (LFP, NMC622, and C65 powder) were analyzed separately, and any background fluorine contribution was subtracted. The values presented are therefore background-corrected.

In the LFP matrix the recovery rate remained consistently around 105 % within the investigated range, with RSDs between 0.3 and 6.3 %. This indicated that the recovery was independent of the ratio of LFP active material to PVdF binder in the sample. Although a slight systematic overestimation was observed, the values remain within an acceptable range.

While the recovery of PVdF in the LFP matrix remained largely independent of the matrix-to-binder ratio, a different behavior was observed for NMC-containing samples. In contrast, samples with high NMC content showed reduced PVdF recovery (90 %), which may indicate matrix-related fluorine losses during combustion, potentially due to interactions of HF with the active material, as it has been discussed in the literature [34,35]. It is also conceivable that the matrix itself affects the combustion efficiency of PVdF. With increasing PVdF content, the recovery values approach 100 %. The RSDs ranged from 0.7 to 3.9 %.

Samples containing carbon black showed a similar but less pronounced trend than NMC containing samples. At higher carbon black contents, PVdF recovery was slightly reduced, suggesting a weaker

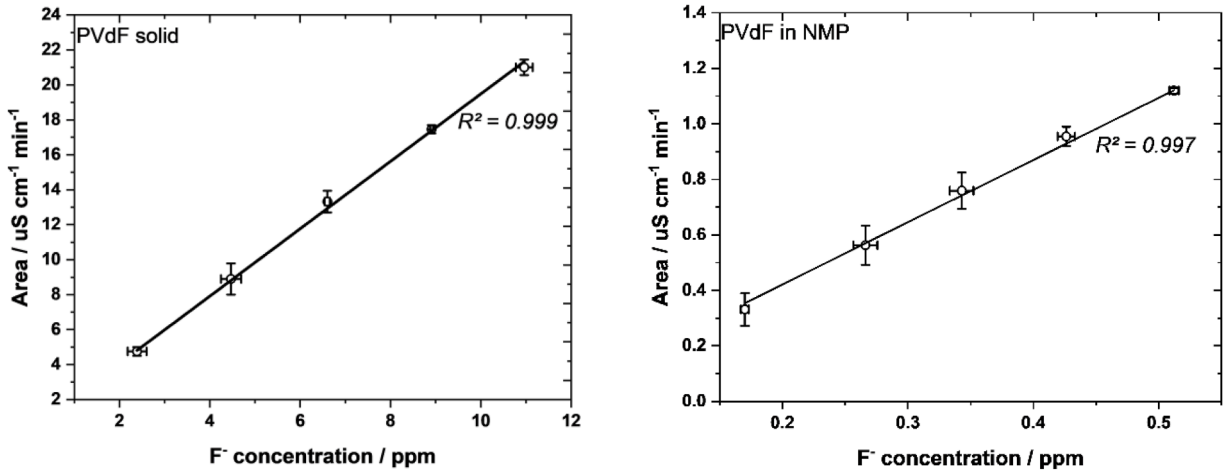

Fig. 3. Calibration of CIC with pure PVdF (left) and PVdF in NMP solution (right).

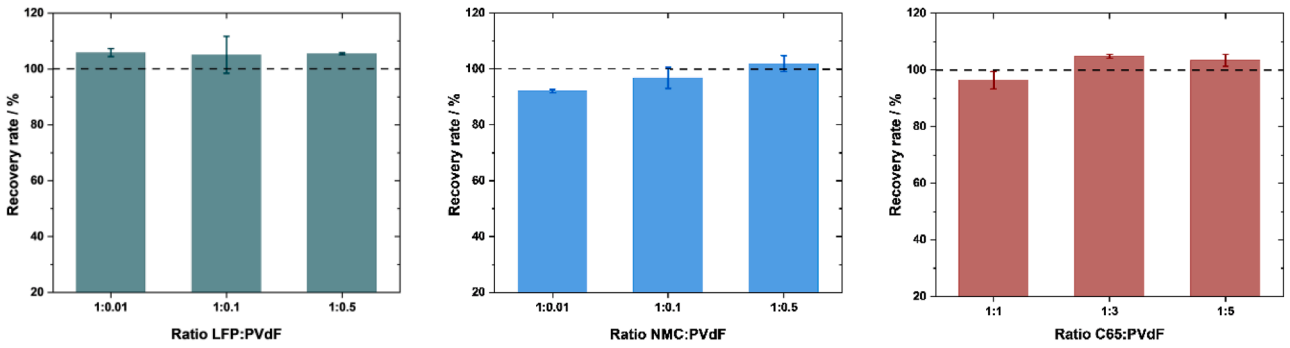

Fig. 4. Effect of LFP (green), NMC622 (blue) and C65 (red) matrix on the PVdF recovery rate.

matrix effect on PVdF combustion efficiency. With increasing PVdF content, the recovery values again ranged between 102 and 103 %, with RSDs of 0.6–3.1 %.

Overall, the results demonstrated that the CIC method enabled reliable quantification of PVdF across different matrix compositions. However, matrix effects were observed at high matrix fractions, particularly in NMC-based materials, indicating that matrix effects should be taken into account. This is especially important for samples with high matrix loadings or low PVdF contents, where the relative contribution of matrix-induced deviations may become more pronounced. Consequently, the use of matrix-matched calibration represents a suitable approach to minimize these effects and enhance quantification trueness.

3.3. Method Application to Black Mass Sample

Within complex black mass matrices, PVdF is not the only fluorine-containing compound present. Other fluorinated compounds, such as residual electrolyte salts (*e.g.,* $LiPF_6$) or SEI-derived residues (*e.g.*, LiF) may also contribute to the overall fluorine signal in CIC measurements. Since CIC determines the total fluorine content rather than selectively detecting PVdF, the calculated PVdF content must be interpreted carefully, particularly for complex recycled materials. Therefore, the potential contribution of non-PVdF fluorine compounds was investigated before applying the method to black mass samples.

To investigate the contribution of other fluorine-containing compounds to the CIC signal, samples of $LiPF_6$, LiF, and anode material (unwashed and washed) were measured. This allowed an assessment of the extent to which residual salts and SEI-derived compounds contribute to the overall fluorine signal, whether these species can be quantitatively detected by CIC, and how effectively a simple washing procedure removes them.

Fig. 5 shows the chromatograms obtained for $LiPF_6$, LiF, and anode material in both unwashed and washed states. All samples exhibited distinct fluorine peaks, demonstrating their contribution to the fluorine signal in CIC measurements. As the anode does not contain a fluorine-containing binder, the detected fluorine species can be attributed exclusively to residual electrolyte and SEI-derived components. For the anode material, a noticeable decrease in peak intensity was observed after washing, indicating that fluorine-containing residues were partially removed. Quantitatively, DMC washing reduced the fluorine signal from 23.95 µg to 9.23 µg, while additional washing with diluted H_2SO_4 decreased the fluorine content to below LOQ. DMC predominantly dissolved $LiPF_6$ and other soluble $Li_xPO_yF_z$ compounds, whereas H_2SO_4 dissolved the less soluble LiF [36,37]. Furthermore, both $LiPF_6$ and LiF are detectable by CIC, with recovery rates of approximately 61 % observed for LiF, which can be attributed to the high stability of LiF [38].

After evaluating potential non-PVdF fluorine contributions, the method was applied to black mass samples. Since the investigated black

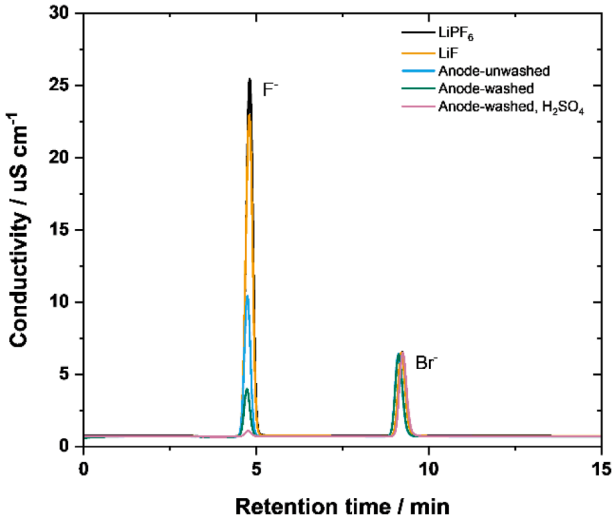

Fig. 5. Chromatograms for the F^- response of other fluorine-containing compounds.

mass samples were predominantly composed of NMC, a matrix-matched calibration based on NMC was applied to account for potential matrix effects. The matrix-matched calibration curve is shown in Fig. 6.

The resulting regression (R^2 = 0.999) for the matrix-matched calibration demonstrated excellent linearity within the investigated concentration range. The LOQ was 1.39 µg PVdF, with RSDs of 1.3–18.0 %,

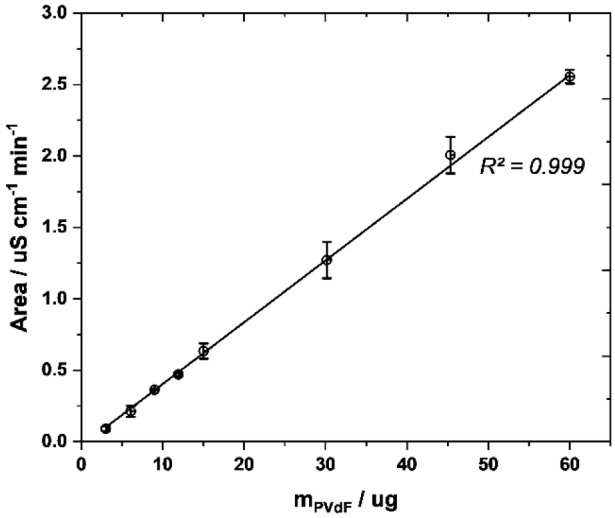

Fig. 6. Matrix-matched PVdF calibration for an NMC matrix.

Table 2
Black mass analysis with PVdF and matrix-matched calibration.

Sample	PVdF in solution	Matrix-matched NMC
BM D1	4.06 ± 0.09 wt%	4.83 ± 0.09 wt%
BM D1 MeOH	2.21 ± 0.13 wt%	2.60 ± 0.16 wt%
BM D1 DMC	-	3.61 ± 0.03 wt%
BM D1 DMC/H_2SO_4	-	2.48 ± 0.04 wt%

confirming the suitability of the method for quantitative fluorine determination. For selected samples, the PVdF content was also determined using the simpler and faster PVdF-in-NMP calibration, enabling a direct comparison between the two approaches. This comparison was applied to an unknown black mass sample, which was examined in both treated and untreated form. The results are summarized in Table 2.

Although both calibration approaches showed consistent trends, the deviation in the quantified values indicated the presence of matrix effects in the sample. For both untreated BM D1 and treated BM D1 MeOH, the matrix-matched calibration yielded systematically higher PVdF contents (4.83 vs. 4.06 wt% and 2.60 vs. 2.21 wt%, respectively). The standard PVdF calibration provided a simple and practical approach for quantification, but it may underestimate the true PVdF content in complex matrices. Nevertheless, the standard calibration remains suitable, particularly in cases where a full black mass characterization is not available or where the additional effort is not justified from a cost–benefit perspective.

It should be noted that CIC determines the total fluorine content in the sample, and the reported PVdF values were calculated under the assumption that all detected fluorine originates exclusively from PVdF. For untreated black mass, however, this assumption is not fully valid, as additional fluorine-containing species such as residual electrolyte salt (*e.g.*, $LiPF_6$) and SEI components are known to be present. Consequently, the PVdF content reported for untreated BM D1 represents an overestimation, as it includes fluorine contributions from non-PVdF sources. The comparison between untreated and treated samples therefore serves primarily to demonstrate the influence of sample pretreatment on the quantification result. During the MeOH treatment, soluble fluorine-containing compounds are partially removed, reducing the non-PVdF fluorine contribution. This is reflected by the decrease in the fluorine content from 4.83 wt% to 2.60 wt%.

Based on the washing experiments performed on anode material, the same procedure was subsequently applied to the black mass sample. DMC washing also reduced the fluorine content from 4.83 wt% to 3.61 wt%, while treatment with diluted H_2SO_4 led to further decrease to 2.48 wt%, indicating the removal of additional inorganic fluorine-containing compounds. To verify that the observed decrease in fluorine content after washing was not caused by PVdF loss, control experiments were performed using pure PVdF. The PVdF powder was subjected to the same washing procedures as applied to the black mass samples. After treatment, the recovered solids were dried to constant mass and analyzed by CIC. The fluorine recoveries ranged from 97.7 % to 98.3 % and remained within the experimental uncertainty of the untreated PVdF reference for all investigated treatments, indicating that the washing procedures did not significantly remove or alter PVdF under the applied conditions. Detailed recovery data are provided in Table S2, Supporting Information. Therefore, the lower fluorine contents observed after washing can mainly be attributed to the removal of soluble electrolyte-derived and/or inorganic fluorinated compounds rather than to PVdF loss. Accordingly, the treated BM D1 samples are expected to more accurately reflect the actual PVdF content in the sample, as further supported by thermogravimetric analysis (TGA) (Fig. S3, Supporting Information).

The effect of varying sample mass on PVdF quantification was investigated using the black mass sample, with sample amounts of 1, 3, and 5 mg (results are provided under Table S1, Supporting Information). The recoveries and repeatability were consistent for 1 and 3 mg samples, while the 5 mg sample yielded slightly lower PVdF values and an increased amount of residue in the combustion boat. These observations suggest that, in the present CIC method, higher sample masses can affect the combustion completeness and the transfer of fluorine to the ion chromatograph. Overall, the results demonstrate that reliable PVdF quantification can be achieved for small to moderate sample amounts, highlighting the robustness of the CIC method for routine and process control measurements. To further validate the method, an in-house produced NMC-based electrode with a known PVdF content was analyzed using matrix-matched calibration. Since the electrode had no prior contact with electrolyte components, the detected fluorine could be attributed exclusively to PVdF, enabling a direct assessment of the method trueness without interference from non-PVdF fluorine sources. The determined PVdF recovery was 97.22 ± 0.89 %, confirming that the matrix-matched calibration compensates for the matrix effects observed in Section 3.2 and provides correct PVdF quantification for real electrode materials.

These results confirm that fluorine-containing compounds other than PVdF contribute to the overall fluorine signal in CIC measurements. The pronounced decrease in fluorine content after DMC washing, and its reduction to below the LOQ following additional H_2SO_4 treatment, demonstrated that inorganic fluorine compounds can be effectively removed by relatively simple washing procedures. Consequently, the total fluorine detected in black mass samples cannot be exclusively attributed to PVdF, particularly in complex matrices where multiple fluorinated compounds may coexist. While such washing steps can significantly reduce contributions from residual fluorinated compounds, careful interpretation of the results remains essential. Therefore, a combination of appropriate calibration strategies and, where necessary, complementary analytical techniques is recommended to ensure reliable PVdF quantification in complex black mass samples. The CIC method is particularly useful for applications such as process control of electrode materials or in direct scrap recycling, where no prior contact with electrolyte components has occurred and rapid, practical analytical methods are required.

4. Conclusion

In this study, combustion ion chromatography was evaluated for the quantification of PVdF in LIB materials, with a focus on the influence of calibration strategy and matrix composition. CIC proved to be a reliable and practical method for PVdF determination, achieving a LOQ of 1.39 µg PVdF for black mass samples using matrix-matched calibration.

Accurate quantification depends primarily on the matrix and on possible fluorine contributions from non-PVdF compounds. Calibration with a pure PVdF standard already provided a reasonable approximation and is sufficient for well-defined or less complex materials, avoiding the need for prior matrix characterization in routine applications. For more complex samples, particularly NMC-rich materials and black mass, matrix-matched calibration is preferable to compensate for matrix effects and prevent underestimation of the PVdF content. Residual electrolyte and SEI-derived compounds (*e.g.*, $LiPF_6$, LiF) were shown to contribute to the total fluorine signal, but a substantial fraction can be removed by simple washing with DMC and/or dilute H_2SO_4, further improving selectivity.

In practical recycling or industrial process contexts, CIC is therefore particularly applicable for routine quality control, process monitoring and comparative assessment of well-characterized input streams. Its main limitations arise for highly heterogeneous black mass samples or materials containing unknown fluorinated compounds, where additional sample pretreatment, matrix-matched calibration, or complementary analytical information may be necessary. Future work should focus on further optimizing sample preparation and extending the approach to other fluorinated binder systems, such as polytetrafluoroethylene.

CRediT authorship contribution statement

Marie Heidler: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Dennis Kessen:** Writing – review & editing, Methodology, Investigation. **Jakob Michael Hesper:** Writing – review & editing, Methodology, Investigation. **Martin Winter:** Writing – review & editing, Supervision. **Simon Wiemers-Meyer:** Supervision, Project administration. **Sascha Nowak:** Writing – review & editing, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2026.467276.

Data availability

Data will be made available on request.

References

[1] R. Schmuch, R. Wagner, G. Hörpel, T. Placke, M. Winter, Nat. Energy 3 (2018) 267–278.
[2] J. Betz, G. Bieker, P. Meister, T. Placke, M. Winter, R. Schmuch, Adv. Energy Mater. 9 (2019) 1803170.
[3] J. Neumann, M. Petranikova, M. Meeus, J.D. Gamarra, R. Younesi, M. Winter, S. Nowak, Adv. Energy Mater. 12 (2022) 2102917.
[4] W. Mrozik, M.A. Rajaeifar, O. Heidrich, P. Christensen, Energy Env. Sci. 14 (2021) 6099–6121.
[5] Y. Zhao, O. Pohl, A.I. Bhatt, G.E. Collis, P.J. Mahon, T. Rüther, A.F. Hollenkamp, Sustain. Chem. 2 (2021) 167–205.
[6] C.M. Costa, J.C. Barbosa, R. Gonçalves, H. Castro, F.J. Del Campo, S. Lanceros-Méndez, Energy Storage Mater. 37 (2021) 433–465.
[7] H. Liu, J. Han, Y. Feng, C. Nong, Y. Liu, L. Cheng, J. Gu, H. Yuan, J. Environ. Chem. Eng. 13 (2025) 120248.
[8] A. Rensmo, E.K. Savvidou, I.T. Cousins, X. Hu, S. Schellenberger, J.P. Benskin, Env. Sci Process Impacts 25 (2023) 1015–1030.
[9] N.D. Tyrrell, Org. Process Res. Dev. 27 (2023) 1422–1426.
[10] L. Terborg, S. Weber, F. Blaske, S. Passerini, M. Winter, U. Karst, S. Nowak, J. Power Sources 242 (2013) 832–837.
[11] M. Wang, K. Liu, J. Yu, Q. Zhang, Y. Zhang, M. Valix, D.C.W. Tsang, Glob. Chall. (Hob. NJ) 7 (2023) 2200237.
[12] H. Zuo, L. Chen, M. Kong, L. Qiu, P. Lü, P. Wu, Y. Yang, K. Chen, Life Sci. 198 (2018) 18–24.
[13] A. Vanderbruggen, N. Hayagan, K. Bachmann, A. Ferreira, D. Werner, D. Horn, U. Peuker, R. Serna-Guerrero, M. Rudolph, ACS EST Eng. 2 (2022) 2130–2141.
[14] A.M. Salces, M.S. Henderson, A.J. Rodríguez-Medina, K. Bachmann, E. Oraby, C. C. Beh, M. Rudolph, J. Eksteen, A. Vanderbruggen, ACS Sustain. Resour. Manag. 2 (2025) 1021–1029.
[15] Y. Wang, X. Yang, Y. Meng, Z. Wen, R. Han, X. Hu, B. Sun, F. Kang, B. Li, D. Zhou, C. Wang, G. Wang, Chem. Rev. 124 (2024) 3494–3589.
[16] Y. Shao, L. Hourdin, J.-Y. Sanchez, C. Iojoiu, C. R., Chim. 28 (2025) 523–541.
[17] J. Li, J. Fleetwood, W.B. Hawley, W. Kays, Chem. Rev. 122 (2022) 903–956.
[18] Z. Mao, Y. Song, A.G. Zhen, W. Sun, Next Sustain. 3 (2024) 100015.
[19] M. Grützke, X. Mönnighoff, F. Horsthemke, V. Kraft, M. Winter, S. Nowak, RSC Adv. 5 (2015) 43209.
[20] X. Mönnighoff, A. Friesen, B. Konersmann, F. Horsthemke, M. Grützke, M. Winter, S. Nowak, J. Power Sources 352 (2017) 56–63.
[21] Y. Akbaş, M. Petranikova, B. Ebin, Sep. Purif. Technol. 376 (2025) 134056.
[22] A. Agustin, M. Manahan, B.G. Sheldon. https://apps.thermoscientific.com/media/cmd/hypersite-events/Pittcon-2014/posters/PN71002_PC2014.pdf, accessed 14.11.2024, 2014.
[23] J.M.N. Aguilar, M.K. Wijayahena, L.S. Running, K. Phatthanawiwat, A. Choodum, J.S. Wallace, D.S. Aga, Env. Sci. Technol. 59 (2025) 3218–3228.
[24] J. Hu, R.E. Cochran, C.M. Grim, N.G. Rumachik, J. AOAC Int. 108 (2025) 367–379.
[25] S. van Wickeren, L. Ihlbrock, C. Peschel, S. Wiemers-Meyer, M. Winter, S. Nowak, J. Chromatogr. A 1756 (2025) 466070.
[26] R. Aro, U. Eriksson, A. Kärrman, I. Reber, L.W.Y. Yeung, iScience 24 (2021) 102968.
[27] B.J. Ross, M. LeResche, D. Liu, J.L. Durham, E.U. Dahl, A.L. Lipson, ACS Sustain. Chem. Eng. 8 (2020) 12511–12515.
[28] C. Chen, Y. Min, Q. Wang, Q. Huang, Waste Manag. 192 (2025) 29–38.
[29] B.M. Basavaraja, N. Rhakho, S.R. Jena, S. Yadav, A. Altaee, M. Saxena, A.K. Samal, Sustain. Chem. Environ. 3 (2023) 100031.
[30] L.D. Ellis, S. Buteau, S.G. Hames, L.M. Thompson, D.S. Hall, J.R. Dahn, J. Electrochem. Soc. 165 (2018) A256–A262.
[31] J.M. Hesper, S. Weigel, J.H. Hintemann, J. Minář, M. Winter, S. Wiemers-Meyer, S. Nowak, ChemSusChem 18 (2025) e202501158.
[32] J.M. Hesper, M. Heidler, N. Fehlings, L.-S. Kemper, V. Kraft, P. Jochems, J. H. Hintemann, V. Naber, D. Stappers, M. Winter, S. Wiemers-Meyer, S. Nowak, J. Power Sources Adv. 39 (2026) 100208.
[33] Y. Miyake, M. Kato, K. Urano, J. Chromatogr. A 1139 (2007) 63–69.
[34] B.J. Ross, M. LeResche, D. Liu, J.L. Durham, E.U. Dahl, A.L. Lipson, ACS Sustain. Chem. Eng. 8 (2020) 12511–12515.
[35] M. Müller, C. Nobis, M. Irmer, M. Fischlschweiger, B. Yagmurlu, Waste Manag. 206 (2025) 115042.
[36] A.C. Resentera, G.D. Rosales, M.R. Esquivel, M.H. Rodriguez, Hydrometallurgy 217 (2023) 106027.
[37] L. Somerville, J. Bareño, P. Jennings, A. McGordon, C. Lyness, I. Bloom, Electrochim. Acta 206 (2016) 70–76.
[38] U. Sharopov, T. Juraev, S. Kakhkhorov, K. Juraev, M. Kurbanov, M. Karimov, D. Saidov, A. Kakhramonov, F. Akbarova, I. Rakhmatshoev, O. Abdurakhmonov, Ion. (Kiel) 31 (2025) 7535–7563.