

Measurement uncertainty assessment for potentiometric determination of trace anionic impurities in graphite post ultrasonic extraction: A bottom-up approach

Harshala Parab ^{1*} and Sangita D. Kumar ^{1,2}

¹Analytical Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai – 400085, India

²Homi Bhabha National Institute, Anushaktinagar, Mumbai - 400094, India

(Received February 24, 2022; Revised April 26, 2022; Accepted May 01, 2022)

Abstract: An evaluation of measurement uncertainty in the analysis of trace level fluoride (F^-) and chloride (Cl^-) impurities in the refractory matrix (graphite) using a bottom-up approach based on the EURACHEM CITAC guide is presented herein. The major uncertainty contribution in the measurement was from calibration slope in case of F^- and calibration intercept in case of Cl^- . The expanded uncertainties calculated by considering the coverage factor ($k=2$) was found to be 7.1 % for F^- and 3.9 % for Cl^- . The higher uncertainty in case of F^- in comparison with Cl^- could be attributed to the presence of F^- in the limiting concentration range. The impact of calibration intercept in the measurement uncertainty for Cl^- analysis can be attributed to the significant contribution of the blank towards the electrode potential. The studies demonstrated the effect of analyte concentration on the measurement uncertainty. The content of analytes along with the expanded uncertainty in the graphite sample were reported as 17.2 ± 1.2 mg/kg of F^- and 3300 ± 130 mg /kg of Cl^- (calculated within 95% confidence level). The statistical concurrence of the results obtained from Ion Selective Electrode (ISE) and Ion chromatography (IC) analyses was confirmed by student's t-test values.

Keywords: Measurement uncertainty; fluoride (F^-); chloride (Cl^-); graphite; ion selective electrode (ISE); ion chromatography. © 2022 ACG Publications. All rights reserved.

1. Introduction

Graphite, an allotrope of carbon, is occurring in nature due to the metamorphism of the sedimentary carbon containing compounds. It has planar sp^2 hybridized carbon atoms in ring structure. Owing to its high electrical conductivity, chemical inertness, corrosion resistance, thermal and mechanical stability, abundance and low cost graphite has widespread industrial applications [1,2]. However, the presence of impurities in graphite makes a visible impact in the properties of the finished product (especially for high value added products). There are reports discussing the effects of impurities in graphite affecting the performance of the intended product. Duan et. al in their recent work, described the effect of purity and proportion of microcrystalline graphite ore on the electrical, mechanical and tribological performance of copper-carbon composites [3]. The authors observed that the performance of the copper-carbon composite

*Corresponding author E-Mail: harshprb@gmail.com; harshala@barc.gov.in

Measurement uncertainty evaluation of trace impurities analysis in graphite

was enhanced with increasing purity of microcrystalline graphite. In another report, Jalili et.al have shown that the silicon based impurities hamper the performance of graphene based devices such as supercapacitor microelectrodes and humidity sensors [4]. They concluded that the utilization of high purity graphite as a precursor is the only route to produce silicon-free graphene in order to further produce the quality products.

The natural graphite obtained by mining is purified using various processes prior to its industrial applications, which include different chemical and physical treatment methods such as chlorination-roasting method, hydrofluoric acid method, alkaline-acid method, flotation, purification at high temperature method etc. [5-9]. The chemical purification method involving use of HCl and NaF is one of the most popular methods as it exhibits high purification efficiency and less impact on the environment. Xie et.al. have discussed that the fixed carbon content of microcrystalline graphite has been improved by using HCl and NaF, which broadens the applications of graphite [5]. Hydrochloric acid is mainly applied to convert the metallic impurities into their respective water soluble chloride salts, whereas the fluoride containing reagents are used to deal with the silicate impurities.

The quantitative analysis of trace impurities in graphite matrix prior to its actual applications is essential, as there is a possibility that the traces of Cl^- and F^- may remain in the graphite matrix after the above mentioned purification processes. These impurities can show adverse effect in the performance of graphite during its usage. For eg., when graphite is used as moderator or structural material for nuclear reactors, the presence of trace level F^- and Cl^- can lead to the corrosion of the components of nuclear reactor system [10].

However, the analysis of graphite has always been a challenging task owing to its refractory nature. Generally, a pre-treatment procedure is required for quantitative extraction of the trace impurities from the refractory sample, which includes pyrohydrolytic extraction, alkaline fusion or microwave assisted acidic dissolution of the matrix [11-13]. This is followed by quantification of the analytes using a suitable instrumental technique. However, the long analysis time, need for many fold dilutions and lower throughput in case of refractory material demand for simpler analytical protocols. To overcome these difficulties, recently we have reported a novel green method for boron-based sample matrix, which involved ultrasound assisted solid-liquid extraction (UA-SLE) of anionic trace impurities from sample matrix followed by its determination using Ion Chromatography (IC) [10]. The developed strategy is devoid of cumbersome sample dissolution or extraction protocols. This sample processing method with minor modifications has been adopted in the present case, for extraction of trace levels of F^- and Cl^- impurities from graphite matrix. The quantification of extracted analytes was performed by potentiometric analysis using ion selective electrodes (ISE). ISE analysis has been chosen considering its accuracy, ease of operation, speed and cost effectiveness.

For any analytical measurement, the accurate and precise results are expected. In this regard, the knowledge of measurement uncertainty for a particular analysis not only assists in judging the quality of the results but it is also significant in risk assessment and decision making during the development of an industrial product. The uncertainty estimation for any measurement definitely improves the data quality, which helps in the decisions related to compliance or non-compliance for a particular product. Therefore, estimation of measurement uncertainty is necessary for any kind of analysis. There are two guides (standard procedures) i.e. EURACHEM CITAC guide and GUM guide on how to estimate the analytical measurement uncertainty [14, 15]. As far as our knowledge, till date there are only two reports related to the estimation of measurement uncertainty of F^- and Cl^- analysis using ISE [16,17]. The scarcity of the information on the estimation of measurement uncertainty related to the ISE analysis makes this study very important and relevant. The main goal of the present study was to estimate the measurement uncertainty in the analysis of trace level F^- and Cl^- in graphite sample using ISE. EURACHEM CITAC guide has been used for the uncertainty calculations in the present measurement using a bottom-up approach. It involved stepwise categorization of the entire analysis, identification of all possible uncertainty sources and calculation of individual uncertainty contribution from each source. The combined measurement uncertainty is then derived by collation of all the uncertainty inputs using the error propagation rules. In addition, the present method was validated by performing the analysis using an alternate instrumental technique such as IC and checking the standard addition recovery in ISE analysis. The statistical agreement of the results from ISE and IC techniques was evaluated using student's t-test. The present report suggests an approach to estimate measurement uncertainty in the analysis of trace impurities in solid refractory matrices using ISEs.

2. Experimental

2.1. Materials and Calibration Standards

The stock standard solution (1.0 mg /mL) for F⁻ and Cl⁻ was prepared by dissolving fixed quantities of the corresponding sodium salts in deionized water. Metrological traceability of the as prepared standard solutions for both F⁻ and Cl⁻ should be established prior to estimation of measurement uncertainty for the present analysis. This was done by analysis of reference standard solution of F⁻ and Cl⁻ (1000 mg/L) supplied commercially by Fluka, which is traceable to SRM from NIST. The measured values for reference standard solutions of F⁻ and Cl⁻ are 999 ± 2 mg/L and 1001 ± 3 mg/L respectively, which are found to be well in agreement with the reference values. The working standard solutions were prepared by successive additions of fixed aliquots of stock standard solution to the 5 mL of solution blank containing ionic strength adjustment buffer to get the desired concentration of working standard. In case of F⁻, TISAB (Total Ionic Strength Adjustment Buffer) with pH 5.5 was employed. The composition of TISAB includes CDTA (trans -1, 2-cyclohexylendinitrilo tetra-acetic acid), sodium chloride, sodium hydroxide and acetic acid (ethanoic acid). The measurements were carried out at the volume ratio of 1:1 between buffer and standard solution. In case of Cl⁻, 0.1 M KNO₃ was used for ionic strength adjustment and the analysis was performed at 1:5 volume ratio between KNO₃ and standard solution. The calibration range for F⁻ and Cl⁻ was 0.1 to 1.0 mg/L and 9.9 to 107.1 mg/L respectively. A Metrohm 692 pH/Ion meter (Herisau, Switzerland) connected to F⁻ or Cl⁻ ISE and Ag/AgCl reference electrode was used for the analysis. Both F⁻ and Cl⁻ ISEs as well as the reference electrode were procured from Metrohm (Herisau, Switzerland). Before actual potentiometric measurements, both the ISE and reference electrode were immersed in 100 mg/L of respective standard solution overnight and rinsed thoroughly with deionised water at the time of measurement. The A.R. grade chemicals from Sigma-Aldrich were used for preparing standard solutions. The glass wares used for the experiments were cleaned with deionized water and oven dried at 60°C. The deionized water (resistivity = 18.3 MΩ cm) for the present studies was taken from a water purification system from Millipore Ltd., USA.

2.2. Sample Analysis

Graphite sample was obtained from a private industry in India. The analysis of graphite comprised of two steps i.e., extraction of analytes by UA-SLE [10] followed by the quantitative determination by ISE method. Initially, 0.25 g of sample (n = 3) was ultrasonicated for 60 min. in aqueous medium using a domestic table - top sonicator at a power of 35 W and frequency of 40 kHz. The solid phase was then separated from aqueous medium by centrifugation for 15 min at 12000 rpm. The aqueous extract was further analyzed for F⁻ and Cl⁻ using ISE. The entire sample processing from UA-SLE, centrifugation to replicate preparation for ISE analysis have been carried out in single container to avoid the error in the analysis. The analysis conditions for both the analytes are illustrated in Table 1.

Table 1. Profile of ISE measurement parameters for graphite sample after ultrasonication

	F ⁻	Cl ⁻
Instrument	Metrohm 692 pH/Ion meter (Herisau, Switzerland)	Metrohm 692 pH/Ion meter (Herisau, Switzerland)
Working Electrode	F ⁻ ISE	Cl ⁻ ISE
Reference electrode	Ag/AgCl	Ag/AgCl
Buffer	TISAB (composed of CDTA +NaOH + NaCl + CH ₃ COOH)	0.1 M KNO ₃
Ratio of buffer: sample solution	1:1	1:5
Total volume (mL)	5	5
Calibration range (mg/L)	0.1-0.5	9.9 -107.1

Measurement uncertainty evaluation of trace impurities analysis in graphite

2.3. Method Validation

Method validation was performed by determining the % recovery of spiked standards in the sample solutions in ISE analysis and also by an alternate IC analysis of the aqueous extract obtained from UA-SLE of the graphite matrix. F^- and Cl^- were analysed by Dionex ICS 5000 system in suppressed conductivity mode. The aqueous extract was passed through 0.22-micron nylon membrane filter prior to analysis. The chromatographic separation was carried out at 30°C with an analytical column - IonPac AS11-HC Dionex (4mm X 250mm) connected to a guard column - IonPac AG11-HC Dionex (4mm X 20mm) using 25 mM NaOH (at a flow rate of 0.5 mL/min) as the mobile phase, followed by detection using conductivity detector (CD) at 35 °C in a suppressed conductivity mode at 31 mA suppressor current. The identification of the respective analyte in the diluted sample solution was performed by comparison of the retention time with that of standard and the quantification was carried out by using a standard calibration curve where the peak areas of the respective standards were taken into consideration.

2.4. Measurement Uncertainty Estimation

The measurement uncertainty associated with the present analysis is estimated systematically following the guidelines of EURACHEM-CITAC guide. The various stages involved in the calculations are given as follows:

Stage 1: Construction of a mathematical equation using experimental variables to define the measurand

The measurand for the present analysis is the concentration of respective analyte in the graphite matrix. It is defined with respect to the experimental variables using a simple equation as given below:

$$C = \left[10^{\frac{(-E+I)}{b}} \times \frac{D \times V}{W} \right] \quad (1)$$

Where

C : Concentration of analyte (F^- or Cl^-) in graphite matrix (mg/kg)

E : Cell potential of the processed sample aliquot during ISE analysis (mV)

I : y-axis intercept of the calibration plot (mV)

b : slope of the calibration curve (mV)

D : Dilution factor

V : Final volume of solution after sample processing (mL)

W : Weight of graphite sample (g)

Stage 2: Illustration of the individual steps of measurement

It is very essential to know the individual steps of the analysis, for better clarity, while calculating the measurement uncertainty. In the present case, the entire analytical protocol can be classified into four sections. Figure 1 gives the pictorial representation of the same and the related steps in each section. The top two sections deal with the standard preparation and instrument calibration and the bottom two sections are associated with the sample processing and analysis.

Stage 3: Determination of specific contributors of measurement uncertainty and calculation of individual error inputs

It is convenient to recognize the individual contributors for measurement uncertainty from Figure 1 which are further shown systematically in the cause and effect diagram (Figure 2). Quantification of the input from all the identified sources towards the measurement uncertainty is done individually, with the help of repeated measurements/using the information from EURACHEM CITAC guide or from the available certificate for the particular instrument or lab ware. The uncertainty calculations are discussed in comprehensive manner in the later section of the manuscript.

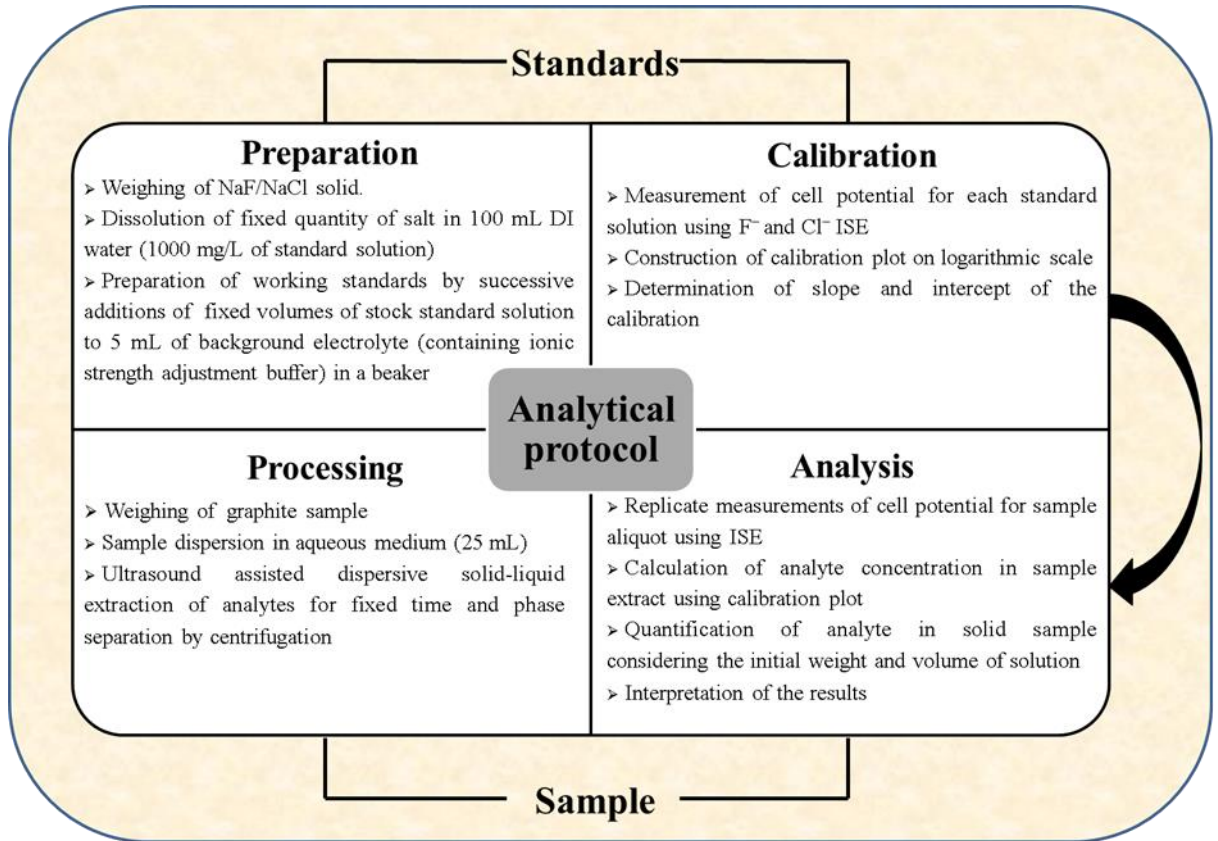


Figure 1. Consolidated protocol for analysis of F⁻ and Cl⁻ in graphite sample

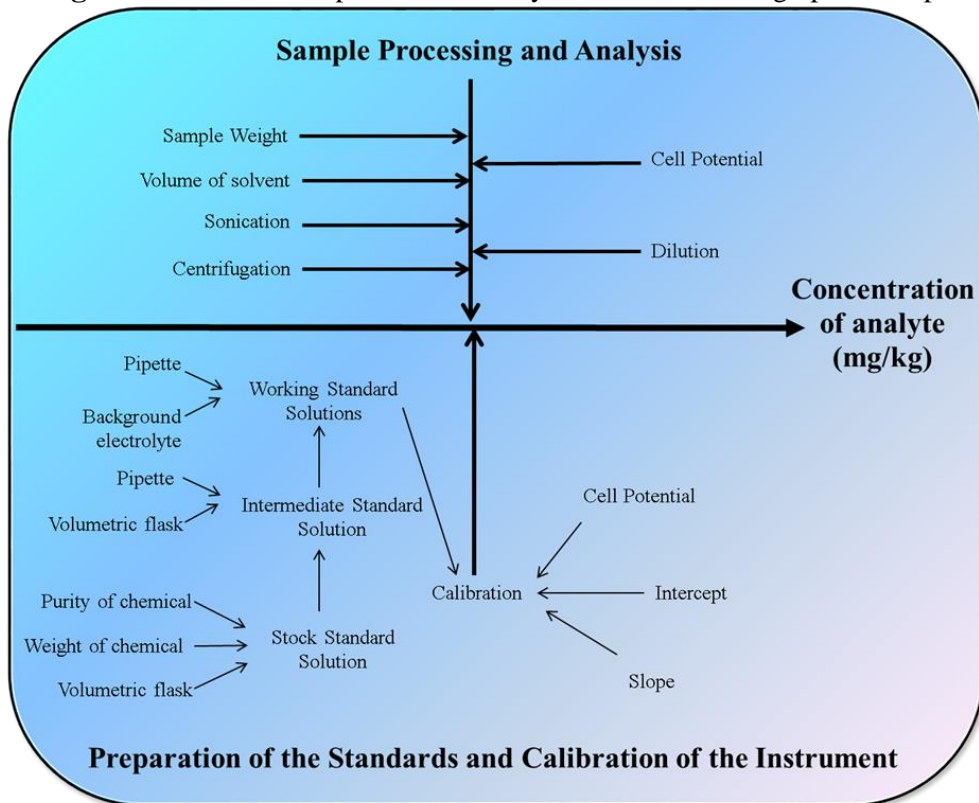


Figure 2. Representation of different factors related to estimation of measurement uncertainty during the analysis of F⁻ and Cl⁻ in graphite: The cause and effect diagram

Measurement uncertainty evaluation of trace impurities analysis in graphite

Stage 4: Collating the uncertainty input from each identified source to calculate combined and expanded uncertainty

The individual uncertainty input from all the identified sources is collated to derive at the combined uncertainty. The expanded uncertainty is further calculated considering the coverage factor (k) =2. The error propagation rules are taken into consideration for the calculations.

Stage 5: Reporting the results

As per the recommendation of EURACHEM - CITAC guide, the result of the analysis should be reported along with the expanded uncertainty inclusive of a statement related to coverage factor and level of confidence.

Stage 6: Designing a plot to correlate the results

A schematic depicting the individual source's contribution towards measurement uncertainty is constructed to highlight the factor giving the major contribution in the combined uncertainty. The calculation and representation of the data in organized manner for each analysis step assists in determining the key parameter in the combined uncertainty.

3. Results and Discussion

The uncertainty estimation in the analysis of graphite matrix for trace anionic impurities (F^- and Cl^-) is challenging as both, the uncertainty associated with the sample pre-treatment (carried out by UA-SLE) and the uncertainty related to ISE measurement need to be considered. The estimation of the uncertainty for the present analysis has been done stepwise, wherein the uncertainty related with standards preparation and instrument calibration is calculated first, followed by the estimation of uncertainty related with processing of the sample and its analysis. The following sections unfold the calculations for the measurement uncertainty in each step of analysis.

3.1. Measurement Uncertainty Related with Preparation of Standards and Calibration

The cause and effect diagram (Figure 2) clearly shows the different parameters contributing to the measurement uncertainty while preparation of the standards and calibration of the instrument. The uncertainty calculations related to the preparation of standard solutions were done using the Eq. (2)-Eq. (7) (where, 'u' corresponds to the relative uncertainty). The uncertainty related to the purity of chemicals such as NaF and NaCl (employed in the preparation of standard solutions), pipette, volumetric flasks and weighing balance were obtained from the manufacturer's certificate. As reported earlier, the uncertainty related to the pipette and volumetric flasks follow the triangular distribution and that related to the purity of chemicals and balance follow rectangular distribution [14]. It is clear from the eq. (2) that the calculation of the uncertainty in the preparation of 1000 mg/L of stock standard solutions of F^- and Cl^- involved the uncertainty contributions from weighing (i.e. from analytical balance calibration combined with weight of the respective chemical), chemicals purity and volumetric flasks. The working standards were prepared by successive additions of either the stock standard (in case of Cl^- analysis) or intermediate standard (in case of F^- analysis) to the ionic strength adjustor electrolyte/ buffer. In the case of preparation of F^- working standards the value of $n = 2, 3, 4$ and 5 corresponds to $0.2, 0.3, 0.4$ and 0.5 mg/L of F^- respectively (eq.5). However, in the case of preparation of Cl^- working standards the value of $n = 2, 3, 4, 5, 6, 7, 8$ and 9 corresponds to $19.6, 29.1, 38.5, 47.6, 56.6, 74.1, 90.9$ and 107.1 mg/L of Cl^- respectively (eq.7).

$$u_{\text{Stock Std for } F^- \text{ or } Cl^- (1000 \text{ mg/L})} = \sqrt{(u_{\text{Weight}}^2 + u_{\text{Purity of chemical}}^2 + u_{\text{Volumetric flask}}^2)} \quad (2)$$

$$u_{\text{Intermediate Std for } F^- (50 \text{ mg/L})} = \sqrt{(u_{\text{Stock Std for } F^-}^2 + (2 \times u_{\text{Pipette}})^2 + u_{\text{Volumetric flask}}^2)} \quad (3)$$

$$u_{\text{F}^- \text{ Working Std 1 } (0.1 \text{ mg/L})} = \sqrt{(u_{\text{Intermediate Std for } F^-}^2 + u_{\text{Pipette}}^2 + (5 \times u_{\text{Pipette}})^2)} \quad (4)$$

$$u_{\text{F}^- \text{ Working Std } n} = \sqrt{(u_{\text{F}^- \text{ Working Std } (n-1)}^2 + u_{\text{Intermediate Std for } F^-}^2 + u_{\text{Pipette}}^2)} \quad (5)$$

$$u_{Cl^- \text{ Working Std } 1 (9.9 \text{ mg/L})} = \sqrt{(u_{\text{Stock Std for } Cl^{-2}} + u_{\text{Pipette}}^2 + (5 \times u_{\text{Pipette}})^2)} \quad (6)$$

$$u_{Cl^- \text{ Working Std } n} = \sqrt{(u_{Cl^- \text{ Working Std } (n-1)}^2 + u_{\text{Stock Std for } Cl^{-2}} + u_{\text{Pipette}}^2)} \quad (7)$$

The uncertainty associated in the preparation of each working standard (as calculated from the above equations) represents the x- axis uncertainty in the calibration curve for that particular standard solution and the corresponding y- axis uncertainty is obtained by the standard deviation associated with the instrumental response i.e. cell potential for each working standard (for n=3). Together, the uncertainty associated with both the x and y variables contribute to the uncertainty related to the instrumental calibration curve. The standard calibration curve for the analytes as shown in Figure 3 were found to be linear with the adjusted determination coefficients (R^2_{adj}) of 0.999 for both F^- and Cl^- . The analyte concentrations were determined using the eq. (1).

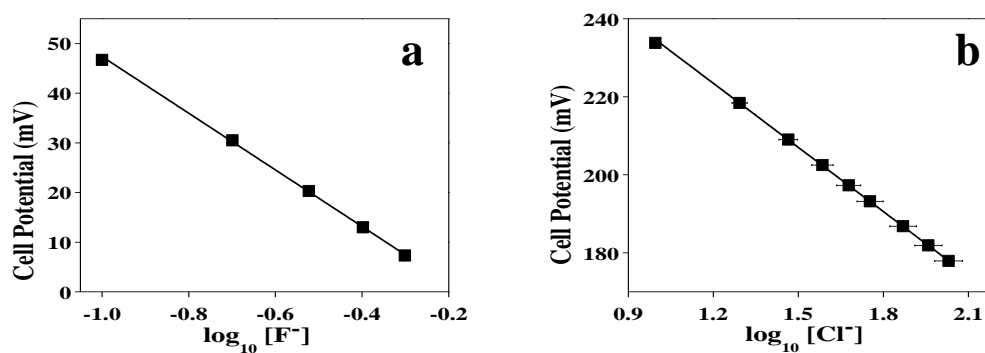


Figure 3. Standard calibration plot for (a) F^- (b) Cl^- from ISE measurements

3.2. Sample Analysis and Method Validation

The chemical purification method of graphite involves the use NaF and HCl. The trace level impurities of F^- and Cl^- may be originated from such purification methods. Herein, the graphite sample was processed in triplicates for extraction of F^- and Cl^- using UA-SLE as reported in the experimental. Ultrasonication facilitated the agitation of sample particles and dispersed them well in aqueous medium by physical vibration using sound waves. UA-SLE efficiently extracted the available F^- and Cl^- impurities from the graphite matrix. The superiority of the UA-SLE sample pre-treatment procedure for analyte extraction over procedures involving highly acidic /alkaline conditions or use of sophisticated techniques such as microwave digestion or pyrohydrolysis has been already established in our earlier work [10] Moreover, the results show that the present simple and green methodology for analyte extraction can be extrapolated to similar type of samples without the need of other harsh treatment methods.

The liquid phase post extraction was analysed for F^- and Cl^- using ion selective electrodes and the results were validated using an alternate IC analysis. The comparison of the results from both the techniques is presented in Table 2. The relative standard deviation (RSD) for the ISE analysis was < 2%. The concentration of F^- and Cl^- in the graphite sample tested by ISE along with standard deviation can be given as 17.2 ± 0.26 and 3270 ± 20 mg/kg, respectively. From Table 2, it is revealed that both the techniques i.e. ISE and IC are in well agreement with each other, which proves the quality of the results obtained using the present method. Apart from alternate analysis, standard addition recovery for the sample has also been checked for validating the present method. It was done by spiking the sample with fixed amounts of F^- and Cl^- standards. (The addition of standards was based on the concentration of the analytes in the original sample). The standard addition recovery was found to be quantitative for both the analytes (Table 2). Figure 4 shows the chromatogram of the aqueous extract of the graphite sample from IC analysis before and after standard addition. F^- and Cl^- were eluted at 6.8 and 10.6 min respectively. Since the F^- concentration in the

Measurement uncertainty evaluation of trace impurities analysis in graphite

sample was in the limiting range, a small hump indicating the presence of F^- was observed in the chromatogram. The enlarged image of the fluoride peak has been shown in the inset for better clarity. On the other hand, a clearly visible peak at a retention time of 10.6 min. indicates the presence of Cl^- in the sample. The recovery of the corresponding spiked standard for each analyte was found to be quantitative (Table 2).

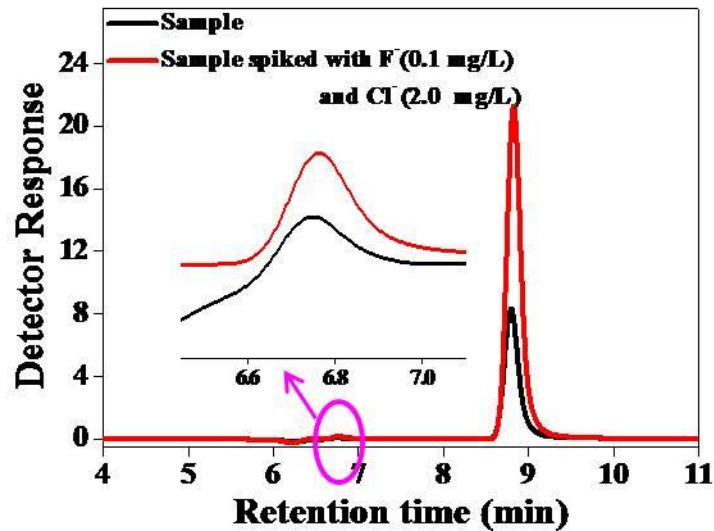


Figure 4. Ion Chromatographic analysis of graphite sample illustrating the presence of analytes and the corresponding standard addition recovery

Table 2. Comparative assessment of graphite analysis results using two different techniques and corresponding standard addition recovery

Analysis Technique	Analyte concentration		Std. addition recovery (%)	
	F^- (mg/kg)	Cl^- (mg/kg)	F^-	Cl^-
Ion Selective Electrode (ISE)	17.2 ± 0.26	3270 ± 20	97	99
Ion Chromatography (IC)	16.7 ± 1.5	3100 ± 159	94	98

*Results rounded off according to ASTM E29-13.

The statistical comparison of results obtained from ISE analysis with those from IC analysis was performed using the student's t-test. The eq. (8) as given below was used to calculate the statistic 't'.

$$t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{\left(\frac{(n_1 - 1)s_{x_1}^2 + (n_2 - 1)s_{x_2}^2}{(n_1 + n_2 - 2)} \right) \times \left(\frac{1}{n_1} + \frac{1}{n_2} \right)}} \quad (8)$$

Where,

x_1, n_1 and s_{x_1} - Individual mean, number of replicate measurements and standard deviation of ISE analysis respectively

x_2, n_2 and s_{x_2} - Individual mean, number of replicate measurements and standard deviation of IC analysis respectively

$n_1 = n_2 = 3$ for the present analysis

$(n_1 + n_2 - 2)$ - Degrees of freedom for the present analysis which has the value 4.

The experimental 't' values in case of both the analytes were determined for 4 degrees of freedom and a significance level of 0.05. The experimental 't' value was found to be 0.68 for F⁻ and 1.83 for Cl⁻, whereas the critical value of 't' was observed to be 2.13 for both. The higher critical 't' value in comparison with the calculated value for both the analytes signifies statistical concurrence of both ISE and IC techniques. Overall, the UA-SLE extraction with ISE determination proved to be a simple, efficient and green protocol as compared to other techniques.

3.3. Measurement Uncertainty Related to the Sample Analysis

The main factors contributing to the uncertainty associated with the sample analysis can be identified clearly from the eq. (1) which include cell potential (i.e instrumental response), calibration functions such as slope and intercept, dilution factor, volume and weight of the sample. The combined uncertainty is estimated by taking into consideration the inputs from individual error sources. It can be mathematically represented as follows:

$$\left(\frac{u_c}{C}\right)^2 = \left(\left(\frac{2.303}{b}\right)^2 u_E^2 + \left(\frac{2.303}{b}\right)^2 u_I^2 + \left(\frac{2.303(-E+I)}{b^2}\right)^2 u_b^2\right) + \left(\frac{u_D}{D}\right)^2 + \left(\frac{u_V}{V}\right)^2 + \left(\frac{u_W}{W}\right)^2 \quad (9)$$

$$u_c = C \times \sqrt{\left(\left(\frac{2.303}{b}\right)^2 u_E^2 + \left(\frac{2.303}{b}\right)^2 u_I^2 + \left(\frac{2.303(-E+I)}{b^2}\right)^2 u_b^2\right) + \left(\frac{u_D}{D}\right)^2 + \left(\frac{u_V}{V}\right)^2 + \left(\frac{u_W}{W}\right)^2} \quad (10)$$

$$U_c = k \times u_c \quad (11)$$

Where

- 'u' - uncertainty related to the particular parameter
- 'u_c' - Combined standard uncertainty for the entire analysis
- 'U_c' - Expanded (absolute) uncertainty for the entire analysis
- k - Coverage factor with the value =2.

From the Eq. (9), it is very clear that systematic determination of u_E , u_I , u_b , u_D , u_V , u_W is essential in estimating the combined uncertainty for the present analysis. 'u_E', the standard uncertainty associated with cell potential of sample aliquot is the standard deviation in the instrumental response derived from the triplicate measurements. The uncertainties related with the calibration functions such as intercept and slope i.e. u_I and u_b are the errors associated with these parameters, which are obtained from the curve fitting parameters. The uncertainty associated with the dilution 'u_D' was calculated by considering the dilution factor of 1.66 and 5 for F⁻ and Cl⁻ respectively. 'u_V', the uncertainty related to the volume have been calculated for 25 mL as the solid sample was dispersed in the same volume. The calculation was similar to that calculated earlier in case of standards. As discussed earlier, 'u_W', the uncertainty related with the weight of sample arise from that of the sample weight and weighing balance. Apart from the factors from Eq. (1), there are certain additional factors which can contribute to the measurement uncertainty such as ultrasonication and centrifugation (as can be seen from the cause and effect diagram). Since the optimized sample pre-treatment protocol from the earlier report has been adapted herein, the contributions from these two processes were observed to be insignificant. The values of the uncertainties for different individual parameters from equation (1) are presented in Table 3. The expanded uncertainty is a product of combined uncertainty and coverage factor (k = 2), which has been calculated within 95% confidence level. The concentrations of analytes in the graphite sample along with the expanded uncertainty were reported as 17.2 ± 1.2 and 3300 ± 130 mg/kg for F⁻ and Cl⁻. The values presented were rounded off according to ASTM E29-13 [18]. Figure 5 illustrates the % contribution of individual parameter in the combined uncertainty for the present ISE measurement. The major contribution of uncertainty was estimated to be from calibration slope (80.8%) in the case of F⁻, and intercept (80.4%) in the case of Cl⁻. The results are in concurrence with earlier reports discussing the effects of calibration functions on the analytical

Measurement uncertainty evaluation of trace impurities analysis in graphite

measurement [19-21]. Apart from these two factors, instrumental response i.e. the cell potential also showed measurable contribution in the combined uncertainty which is generally observed in most of the instrumental analyses. On the contrary the factors such as weight, volume and dilution, showed negligible impact in the combined uncertainty. The % expanded uncertainties calculated by considering the coverage factor was found to be 7.1 for F^- and 3.9 for Cl^- . The higher % expanded uncertainty in the case of F^- in comparison with Cl^- could be attributed to the lower concentration of F^- in graphite sample. This is also supported by the observation of major uncertainty contribution from calibration slope for F^- as it reflects the sensitivity of a particular analytical measurement. The major role of calibration intercept in the measurement uncertainty for Cl^- can be attributed to the contribution of the blank towards the electrode potential. The studies revealed that the concentration levels of the analytes (i.e. impurities in the present case) affect the measurement uncertainty significantly. Similar observations have been obtained by Remya Devi et. al. during the analysis of gold in copper concentrate [22]. They noted that measurement uncertainty increases with decrease in the analyte concentration. This pattern has also been established in the Horwitz Function. Horwitz observed that as the concentration of the analyte reduces over two orders of magnitude, the relative standard deviation of reproducibility increases by a factor of two [23,24]. According to him, this pattern in the relative standard deviations persisted at least down to sub-ppm levels. Thus the dependency of the uncertainty function on the concentration of the analyte (impurities) is clear from the present studies.

Table 3. Summary of uncertainty calculations in the measurement of F^- and Cl^- in graphite sample

Analyte	Factor contributing to measurement uncertainty	Numerical Value	Standard Uncertainty	Contribution to combined uncertainty	
				(mg/kg)	%
Fluoride	Cell potential (mV)	46.4667	0.3786	0.2614	43.0
	Intercept (mV)	-9.68E+00	0.3451	0.2419	39.7
	Slope (mV)	-57.0583	0.7193	0.4917	80.8
	Dilution factor	1.6667	0.003849	0.03982	6.5
	Sample solution volume (mL)	25	0.01633	0.01126	1.9
	Sample weight (g)	0.25	8.164E-06	0.0005623	0.1
	Analyte concentration (mg/ kg)	17.2439			
	Combined uncertainty (mg/ kg)	0.6085			100.0*
	Expanded uncertainty (mg/ kg)	1.2171			
Chloride	Cell potential (mV)	228.0333	0.1528	20.9060	33.1
	Intercept (mV)	289.1933	0.3674	50.8389	80.4
	Slope (mV)	-54.7914	0.1955	30.2148	47.8
	Dilution factor	2.5	0.005774	7.5452	11.9
	Sample solution volume (mL)	25	0.01633	2.1341	3.4
	Sample weight (g)	0.25	8.164E-06	0.1067	0.2
	Analyte concentration (mg/ kg)	3267.1817			
	Combined uncertainty (mg/ kg)	63.2147			100.0*
	Expanded uncertainty (mg/ kg)	126.4293			

*The value combined uncertainty has been obtained by propagation of individual contributed uncertainties.

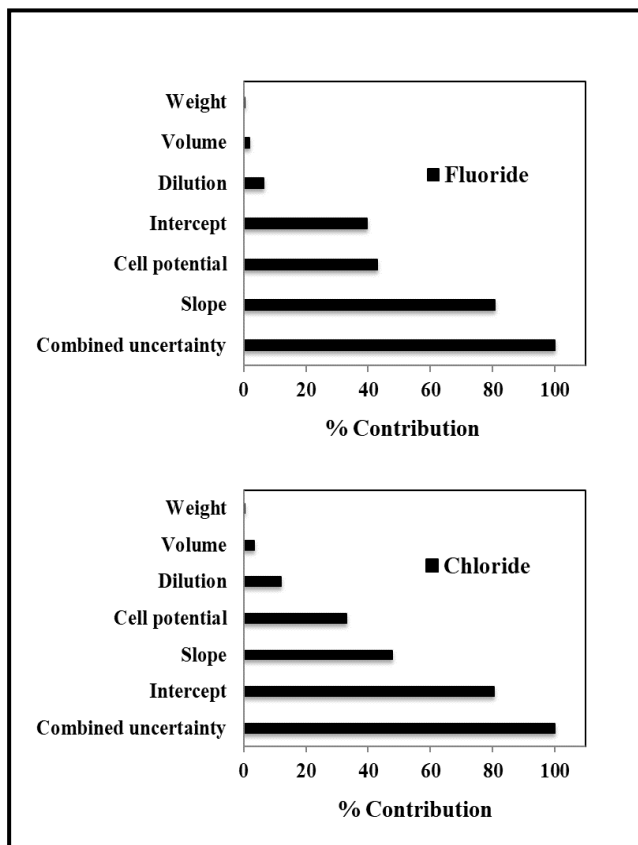


Figure 5. Bar plot elucidating the % contribution of specific sources towards the combined uncertainty in the ISE measurement of F^- and Cl^- from graphite

4. Conclusions

The present studies demonstrated the bottom-up approach for estimating the measurement uncertainty by following the EURACHEM CITAC guide for potentiometric analysis of trace anionic impurities (F^- and Cl^-) in graphite matrix post ultrasonic extraction. The uncertainty evaluation of the entire process involved recognizing the experimental factors possibly contributing to the measurement uncertainty, through a cause and effect diagram and quantifying their contribution. The concentration of F^- and Cl^- in the graphite sample along with the expanded uncertainty was reported as 17.2 ± 1.2 and 3300 ± 130 mg/kg respectively. The expanded uncertainty for the measurement was found to be higher (7.1 %) for F^- than for Cl^- (3.9 %) possibly attributed to the lower concentration of F^- in the sample. The major uncertainty contributors were identified as the calibration functions (slope and intercept) and the response from the instrument. Instrumental response was also found to be one distinct uncertainty factor contributing to the combined uncertainty of the analysis. The effect of analyte concentration on the measurement uncertainty was clearly observed in the present case. The RSD for the present analytical strategy was $< 2\%$. The potentiometric analysis results were found to be precise and accurate when validated with IC analysis and standard addition recovery tests. The competence of the ISE analysis with IC analysis was proved by student's t-test.

Acknowledgements

The authors would like to thank Dr. C. N. Patra, Head, Analytical Chemistry Division and Dr. A. K. Tyagi, Director, Chemistry Group, BARC for their constant support. Thanks are also due to Dr. Remya Devi P.S. and Mrs. N.S. Shenoy for the technical discussions during the studies.

Measurement uncertainty evaluation of trace impurities analysis in graphite



Harshala Parab: [0000-0002-8536-3067](https://orcid.org/0000-0002-8536-3067)

Sangita D. Kumar: [0000-0002-8500-3969](https://orcid.org/0000-0002-8500-3969)

References

- [1] H.O. Pierson (1993). Handbook of carbon, graphite, diamonds and fullerenes: properties, processing and applications. Noyes Publications, Park Ridge, New Jersey.
- [2] A. D. Jara, A. Betemariam, G. Woldetinsae and J. Y. Kim (2019). Purification, application and current market trend of natural graphite: A review, *Int. J. Min. Sci. Technol.* **29**, 671-689.
- [3] S. Duan, X. Wu, X. Min, Z. Huang, T. Yue, W. Yue, M. Fang and Y. Liu (2019). Effect of purity and proportion of microcrystalline graphite ore on the electrical, mechanical and tribological performance of copper carbon composites, *Mater. Res. Express.* **6**, 125604.
- [4] R. Jalili, D. Esrafilzadeh, S. H. Aboutalebi, Y. M. Sabri, A. E. Kandjani, S. K. Bhargava, E. D. Gaspera, T. R. Gengenbach, A. Walker, Y. Chao, C. Wang, H. Alimadadi, D. R. G. Mitchell, D. L. Officer, D. R. MacFarlane and G. G. Wallace (2018). Silicon as a ubiquitous contaminant in graphene derivatives with significant impact on device performance, *Nature Commun.* **9**, 5070.
- [5] W. Xie, Z. Wang, J. Kuang, H. Xu, S. Yi, Y. Deng, T. Cao and Z. Guo (2016). Fixed carbon content and reaction mechanism of natural microcrystalline graphite purified by hydrochloric acid and sodium fluoride, *Int. J. Miner. Process.* **155**, 45-54.
- [6] P. Ge, H.-J. Wang, J. Zhao, L. Xie and Q. Zhang (2010). Preparation of high purity graphite by an alkaline roasting-leaching method, *Carbon* **48**, 2123-2124.
- [7] H. Wang, Q. Feng, X. Tang and K. Liu (2016). Preparation of high-purity graphite from a fine microcrystalline graphite concentrate: Effect of alkali roasting pre-treatment and acid leaching process, *Sep. Sci. Technol.* **51**, 2465-2472.
- [8] H. Wang, Q. Feng, K. Liu, K. Zuo and X. Tang (2018). A novel technique for microcrystalline graphite beneficiation based on alkali-acid leaching process, *Sep. Sci. Technol.* **53**, 982-989.
- [9] S. C. Chelgani, M. Rudolph, R. Kratzsch, D. Sandmann and J. Gutzmer (2016). A Review of graphite beneficiation techniques, *Miner. Process. Extr. Metall.* **37**, 58-68.
- [10] H. Parab, P. S. Remya Devi, J. Ramkumar, N. Shenoy and S. D. Kumar (2019). Uncertainty budget for the ion chromatographic determination of fluoride and chloride in nuclear grade boron carbide and elemental boron employing ultrasound-assisted dispersive solid-liquid extraction, *J. Liq. Chromatogr. Relat. Technol.* **42**, 629-637.
- [11] M. V. Balarama Krishna, S. V. Rao, Y. Balaji Rao, N. S. Shenoy and D. Karunasagar (2014). Development of a microwave-assisted digestion method for the rapid determination of chloride and fluoride in nuclear-grade boron carbide powders, *Anal. Methods.* **6**, 261-268.
- [12] S. D. Kumar, K. Venkatesh and B. Maiti (2004). Determination of chloride in nuclear-grade boron carbide by ion chromatography, *Chromatographia* **59**, 243-245.
- [13] S. Jeyakumar, V. V. Raut and K. L. Ramakumar (2008). Simultaneous determination of trace amounts of borate, chloride and fluoride in nuclear fuels employing ion chromatography (IC) after their extraction by pyrohydrolysis, *Talanta* **76**, 1246-1251.
- [14] S. L. R. Ellison and A. Williams (Eds). (2012). EURACHEM/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition, ISBN 978-0-948926-30-3.
- [15] JCGM 100:2008. Joint Joint Committee for Guides in Metrology. Evaluation of measurement data - Guide to the expression of uncertainty in measurement (GUM). https://www.bipm.org/utls/common/documents/jcgm/JCGM_100_2008_E.pdf
- [16] A. R. Sousa and M. A. Trancoso (2005). Uncertainty of measurement for the determination of fluoride in water and wastewater by direct selective electrode potentiometry, *Accred. Qual. Assur.* **10**, 430-438
- [17] D. Štepec, G. Tavčar and M. Ponikvar-Svet (2019). Measurement uncertainty evaluation and traceability assurance for total fluorine determination in vegetation by fluoride ion selective electrode, *J. Fluor. Chem.* **217**, 22-28.
- [18] ASTM E29-13 (2019). Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications. doi:10.1520/E0029-13R19.
- [19] P. S Remya Devi, A. C. Trupti, A. Nicy, A. A. Dalvi, K. K. Swain, D. N. Wagh and R. Verma (2015). Evaluation of uncertainty in the energy dispersive X-ray fluorescence determination of platinum in Alumina, *Anal. Methods* **7**, 5345-5351.
- [20] J. N. Miller and J. C. Miller (2010). Statistics and chemometrics for analytical chemistry. Sixth edition, Pearson Education Limited, page no.119,

Parab and Kumar, *J. Chem.Metrol.*X:X (202X)XX-XX

- [21] P. S. Remya Devi, T. A. Chavan, S. S. Shitole, P. M. Gawade and K.K. Swain (2021). Insights into the inter-element effects in the EDXRF determination of zirconium in binary aqueous solutions via the calibration method, *Anal. Chem. Lett.* **11**, 83-101.
- [22] P. S Remya Devi, A. A. Dalvi, K. K. Swain and R. Verma (2015). Comparison and statistical evaluation of neutron activation methodologies for the determination of gold in copper concentrate, *Anal. Methods* **7**, 3833-3840
- [23] W. Horwitz. L. R. Kamps and K. W. Boyer, (1980) Quality assurance in the analysis of foods and trace constituents, *J. Assoc. Off. Anal. Chem.* **63**, 1344-1354
- [24] The amazing Horwitz function, (2004) Edited by Thompson M., AMC technical Brief No.17, Royal Society of Chemistry (amc\amctb\statssc\horwitztb_v2.doc 14/07)

A C G
publications

© 2022 ACG Publications