

Reducing occupational risks and greening a traditional sample treatment of industrial fluorine containing-materials by application of design of experiments

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Abstract: - Despite the new technological advances, some traditional methodologies concerning wet chemistry must be used as reference methods when dealing with complex matrices or when no certified reference materials are available. In this context, Willard-Winter distillation is nowadays still employed as a reference technique for fluorine extraction in day-to-day analysis. However, this procedure requires strong acid mixtures, increasing waste treatment procedures/costs and the potential risks associated with their use.

The present work reports the application of design of experiments (DoE) to improve the analytical methodology of reference for fluorine extraction through Willard-Winter distillation by substituting perchloric acid. Variables affecting the sample treatment of fluorine-containing compounds, anhydrite, fluorspar, cryolite and aluminium fluoride were studied to ensure complete dissolution and total extraction of fluorine.

Volume of sulfuric acid, sample amount, volume of distilled solution including volume of melt and amount of NaOH for fluorspar and the extended fluoroaluminate compounds were the variables studied. Predicted experimental conditions were performed and validated in the target compound, obtaining fluorine concentrations comparable to those obtained by the reference methodology.

By this modified approach, not only harmful effect of manipulation of perchloric acid is reduced but also costs of the analytical procedure do so. Besides, a greener performance is achieved by avoiding chlorinated species, reducing waste dangerousness and its treatment.

Key-Words: - fluorine distillation, anhydrite, fluorspar, cryolite, aluminium fluoride, fluorine analysis, design of experiments

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1 Introduction

Innovation and development of new fluorinated chemicals and its applications situates fluorine industry in a privileged and little-known position though its great importance in many areas of daily life. The increase of hydrofluoric acid in the market (valued at US\$1,839.1 million in 2022) gives an idea of the widespread demand existing for its use in different fields (e.g. petroleum refining, glass treatment, metallurgic industry, production of electronics, pharmaceuticals and agrochemicals). Both economic aspect and tithing applicability make the fluoride chemical industry of special relevance in end-users' industry and technological research centers [1,2].

Likewise, there is an increased concern to improve analytical procedures as one of the biggest challenges from the safety and environmental point

of view while simultaneously creating economic, environmental value for all employees and society. In this sense, hazardous substances are the main target to be replaced by others less toxic and less dangerous to reduce risks and complicated treatment of hazard residues [3,4].

Fluorinated compounds are synthesized by hydrofluoric acid, which is mainly produced from the mineral fluorspar, also called fluorite. The reaction of fluorspar with sulfuric acid in excess produces HF and anhydrite, which is a by-product used for further applications, mainly in the cement industry [5]. The demand for hydrofluoric acid is focused on the electronic industry for the manufacture of silicon-based semiconductor devices, on nuclear stations to achieve ²³⁵U growing process, on fluororganic/fluoropolymers compounds and on the aluminium manufacture where aluminium fluoride

and cryolite compounds play an important role in the so-called: Hall-Héroult electrolysis process [1,6-11].

Different methodologies have been proposed to achieve the extraction of fluorine from the sample and its further quantification. Distillation, pyrohydrolysis and alkaline fusion were the most used for sample treatments, whereas potentiometric, volumetric or spectrophotometric measurements were the most usual methods for fluorine determination [12-20]. Furthermore, instrumental breakthroughs lead to the implementation of faster, simpler alternatives such as X-ray fluorescence spectroscopy, with good reproducibility results for the direct analysis of fluorine from solid samples without any pretreatment of the sample [21]. However, these methods have not replaced the official methodologies where Willard-Winter distillation is still the selected procedure for the extraction of fluorine in fluor spar, aluminium fluoride and cryolite [22-24].

In HF factory laboratories, quality control analysis are performed routinely to ensure the adequate quality of raw materials and the best performance of the reaction in intermediate products to fulfill customers' requirements in final products. Considering the current policies committed to ensure safety and health/environment protection, this study deals with the substitution of perchloric acid for sulfuric acid to extract and analyze fluorine from the target compounds, anhydrite, fluor spar, cryolite and aluminium fluoride.

For this aim, a chemometric study using design of experiments (DoE) was conducted to find the best experimental conditions for fluorine recovery, when the mixture of perchloric/phosphoric acid is replaced by sulfuric acid as the most suitable. A first screening study was carried out to select the main variables before the achievement of the most suitable experimental conditions in the optimization phase applying central composite design. Once the new experimental conditions were fulfilled using sulphuric acid, the new modified procedure was validated and compared to those from reference ones to check the viability for its implementation in routine analysis.

2 Experimental

2.1 Reagents and solutions

Internal reference compounds (anhydrite, fluor spar, cryolite and aluminium fluoride) were provided by the company DDF, S.A. (Ontón, Spain) with a

particle size < 350 μm . Sodium hydroxide for the alkaline fusion and phosphoric (85%), perchloric (70%) and sulfuric acids (95%) as fluorine extracting agents were used in the distillation process supplied by Merck (pro analysi quality, Darmstadt, Germany). Silica (chromatography quality) with a diameter pore between 0.04 and 0.063 mm was used as silicon source for fluorine distillation and provided by Merck (Darmstadt, Germany).

Distilled solutions were neutralized at pH 6.8 – 7.0 before potentiometric determination by using a solution of sodium hydroxide 5.0 M and bromothymol blue solution (0.04 % as indicator supplied both by Panreac Química S.A. (Barcelona, Spain).

Sodium citrate (0.1 M) and sodium chloride (1.5 M) solutions, both supplied by Merck (Darmstadt, Germany), were used as TISAB buffer (Total Ionic Strength Adjuster Buffer). This buffer solution was used to set pH values' solutions before potentiometric determination of fluoride, to maintain the ionic strength at a constant and high value and to form complexes of interfering anions. Calibration curves were performed by serial dilution from the stock solution of sodium fluoride (1000 $\mu\text{g/mL}$, quality Titrisol) provided by Merck (Darmstadt, Germany).

Distillation performance, buffer and standards solutions were prepared with purified water from a Milli-Q Element A10 water system (Millipore, Milford, MA, USA).

2.1 Reference methodology

The methodologies described below are routinely used in the fluorine industry DDF, SA and are considered as the reference methods in this study. A sample pretreatment by alkali fusion is performed not only in aluminium derivatives, which are insoluble in acidic solutions but also, in fluor spar to ensure fluorine extraction.

Sample pretreatment consisted of a first melting step by an alkali fusion before fluorine distillation. This step was carried out in a nickel crucible where samples were deposited between a sand of 5 g NaOH. The crucible is covered and introduced in the oven at 500 $^{\circ}\text{C}$ for 15 minutes until total alkaline fusion. Then, the mixture was dissolved in high-purity water until room temperature, transferred into a 250 mL calibrated flask and finally diluted with high-purity water.

The distillation process was performed by introducing the sample amount (in the case of anhydrite) or 50 mL of the alkaline solution (fluorspar and aluminium derivatives), 60 mL of a mixture of perchloric acid and phosphoric acid (50%), 0.5 g of silica to promote fluoride distillation as a combination HF:SiF₄ according to Kleboth's and Dahle's works[25,26], and 200 mL distilled water. The distillate was collected into a vessel up to 800 mL that contained previously 100 mL of distilled water, **Table 1**.

Table 1. Experimental values of reference methodology for the sample pretreatment of anhydrite, fluorspar, cryolite and aluminium fluoride. (*NA: Not applicable).

Variables	Anhydrite	Fluorspar, cryolite and aluminium fluoride
V _{ac} (mL)	60	60
V _{des} (mL)	800	800
m (g)	2.0	0.5-0.6 (fluorspar) 0.4-0.5 (cryolite) 0.3-0.4 (AlF ₃)
V _{melt} (mL)	NA*	50
m _{NaOH} (g)	NA*	5+5

Potentiometric calibration curves were built at the potential defined for the fluoride content according to the Nernst equation. Calibration curves were prepared from 1 mg/L to 10 mg/L for anhydrite, 10 to 50 mg/L for fluorspar and cryolite and, from 30 to 70 mg/L for aluminum fluoride. The stock solutions were prepared in 100 mL calibrated flasks that contained 50 mL of 0.1 M TISAB solution. The measurement of samples was performed by mixing 10 mL of distilled solution and 10 mL of TISAB. After fluorine measurement by ISE-F, fluoride recovery (%) was calculated as follows:

$$F \text{ (g/100g sample)} = (f * C_F * V_{des}/m) * 100 \text{ Eq.1}$$

f: factor (anhydrite 0.002; fluorspar and fluoroaluminate species: 0.5/V_{melt})

C_F: fluoride concentration obtained by interpolation from the calibration curve

V_{des}: volume of distillate

m: sample amount

2.1 Chemometric optimization

2.4.1. Variables and response selection

The start point of the chemometric optimization was stated on defining the response and the most significant variables that may affect the distillation process. In this work, the fluorine content expressed as fluoride (%) was considered the response in all the target compounds except for fluorspar, which was expressed as CaF₂ (%). The volume of sulfuric acid (V_{ac} mL), sample amount (m, mg) and volume of distilled solution (V_{des} mL) were the variables studied, including the volume of melt sample (V_{melt} mL) and amount of NaOH (m_{NaOH}, g) for fluorspar and the extended fluoroaluminate compounds which are insoluble in acidic solutions as it was above mentioned.

The volume of sulphuric acid was the main variable selected regarding the goal of this research. The volume of distillate was studied since it is related to the analysis time and the volume of waste generated. Sample amount and volume of melt were chosen because they are key variables in the sample treatment. More concretely, the volume of melt was chosen for those compounds requiring previous solubilization via alkali fusion whose neutralization effect may affect the free acid in the solution to extract the fluorine from the matrix. Other parameters such as flow, temperature distillation and distillates' pH values were monitored during the distillation process.

2.4.2. Screening phase

A screening step was performed to study the effects of the variables by a full factorial design (2^k+ 2) for anhydrite and a fractional factorial design (2^{k-1}+ 2) for the rest of the target compounds. The screening phase was applied with two replicas in the central point and using high, medium and low levels of variables.

Fluorine recovery values were fitted to a mathematical model using a multiple regression algorithm, based on ordinary least squares regressions. These regression equations (one per analyte) were statistically evaluated by analysis of ANOVA at 5% significance level, to estimate and determine effects and interactions.

This analysis compares the variance of the responses with the residual variance, which summarizes experimental error. These ratios have a statistical distribution, which is used for significance testing. Effects were declared significant (+/-) or non-significant (NS) regarding p-values. Variables with

p-values lower than 0.05 (significance level of 5%) were considered “statistically significant”. The grade of significance increased (++/—) when p-value < 0.01 [27,28].

Model suitability was checked regarding the obtained R^2 (percentage of variance explained) for each response model and studying residuals distribution. In all cases, R^2 values showed a good fit and residuals’ distributions did not diverge significantly from the normal distribution.

Five blanks were evaluated along each factorial design as a quality control to check the suitability of the whole procedure, ensuring that no fluorine was recovered after performing experiments at different conditions.

2.4.2.1. Anhydrite

Anhydrite was the simplest sample to study since it does not require an alkaline fusion step. A full factorial design was carried out with three variables: volume of sulfuric acid (V_{ac} mL), sample amount (m, mg) and volume of distilled solution (V_{des} mL). A total of eight experiments (2^3) including two replicas of central point were randomly performed, **Table 2**.

Table 2. Variables and intervals of variables at low (-1), medium (0) and high (+1) levels studied in the screening design corresponding to anhydrite, fluorspar and the target fluoroaluminate compounds. (*NA: Not applicable).

Variable	Anhydrite			Fluorite			Fluoroaluminate compounds		
	-1	0	1	-1	0	1	-1	0	1
V_{ac} (mL) A	10	30	50	40	60	80	40	60	80
V_{des} (mL) B	200	400	800	800 (fixed)			800 (fixed)		
m (g) C	0.3	1.2	2.0	0.2	0.6	0.80	0.2	0.45	0.7
V_{melt} (mL) D	NA*	NA*	NA*	20	50	80	5+5 (fixed)		
m_{NaOH} (g) E	NA*	NA*	NA*	5+5 (fixed)			3.0	5.0	7.0

Some limitations were found when experiments were performed using less than 40 mL of acid and collecting 800 mL. In these conditions, the distillation temperature overcame 140 °C and the pH value of the distillate solution was lower compared to the reference’s one. These observations may be explained by the presence of other acid than hexafluorosilicic acid in the distillate, as it was reported by Dahle et col. [29]. When the temperature exceeds 140 °C in the distillate, sulfuric acid decomposition to SO_3 is produced, which explains the low pH values of those distillates. Moreover, technical problems arose when employing 10 mL of

sulphuric acid by resistance overheating to the point of breaking the covered glass.

2.4.2.2. Fluorspar and fluoroaluminate compounds

A fractional factorial design was selected in this case considering a compromise between the laborious analysis for fluoride determination and the additional pretreatment step via alkali fusion. The alkali fusion is crucial to achieve dissolution but at the same time, reduces the free acid in the distillator for fluorine extraction. Accordingly, the volume of melt solution and mass of NaOH were the selected variables to take into account in the screening phase but studied separately. The volume of melt was included in the fluorspar design and the mass of NaOH in the cryolite design.

A total of twelve experiments ($2^{3-1} + 2*3+2$) with two replicas in the central point were performed. The volume of sulfuric acid (V_{ac} mL), sample amount (m, mg) and volume of melt solution (V_{melt} mL) were the variables studied in the fluorspar screening phase. And the volume of sulfuric acid (V_{ac} mL), sample amount (m, mg) and volume of NaOH (V_{NaOH} mL) in the cryolite screening phase, **Table 2**.

Technical problems were observed in the case of fluorspar, when the second replica of the central point was performed. Distillation ran irregularly causing resistance overheating till the point of breakage of the covered glass.

Based on the company’s experience with fluoroaluminate compounds analysis, it was assumed that the overall information obtained from the screening phase of fluorspar and cryolite may be extrapolated to aluminium fluoride. For this reason, a screening phase of aluminium fluoride was not conducted before CCD for the optimization phase.

2.4.3. Central composite design, CCD

The CCD was performed to evaluate the response as defined previously but excluding variables of lacked significance among those studied in the screening phase. The CCD allows to model surface responses with a number of experiments equal to (2^k+2k+n) , with k the number of variables and n the number of extra points at the central point of the design. A CCD consisting of a cube samples (2k) with star points ($2 \times n$) placed at $\pm\alpha$ from the central point of the experimental domain. The axial size (α) was 1.68 which establishes the rotatability condition.

The five-level CCD parameter variations and consequent responses conduct fitting of a quadratic model to the data. For an experimental design with

three variables, the model including linear, quadratic and cross terms can be expressed as:

$$Y = \beta_0 + \beta_A X_A + \beta_B X_B + \beta_C X_C + \beta_{AB} X_A X_B + \beta_{AC} X_A X_C + \beta_{BC} X_B X_C + \beta_{AA} X_A^2 + \beta_{BB} X_B^2 + \beta_{CC} X_C^2 \text{ Eq. 2}$$

Where Y is the response to be modelled, β is the regression coefficients and X_A , X_B and X_C represent sample amount (A), volume of acid (B) and volume of melt (C), respectively.

Upon the basis of the obtained responses, a multiple linear regression model (MLR) for each response was defined by the program based on ordinary least squares regression, and evaluated by ANOVA to estimate and determine effects and interactions. To select the optimal conditions, response surface plots were built based on the adjustment parameters obtained after carrying out ANOVA analysis.

Model suitability was checked regarding the percentage of variance explained for each response and verifying the normality distribution of residuals. Once the model's suitability was checked, response surfaces were plotted in three-dimensional space and optimal values were found according to each response surface [30].

Intervals of variables studied in the optimization phase with a central composite design (CCD) for each variable are shown in **Table 3**. In all cases, the explained variance (R_2) values were adequate, greater than 92.0% and distributions of residuals were significantly random.

Table 3. Variables and intervals of variables in the optimization phase with a central composite design (CCD) at (± 1), star ($\pm\alpha$) and center (0) levels. (NA: Not applicable).

Variable	Anhydrite			Fluorspar and fluoroaluminate compounds		
	$-\alpha$	0	$+\alpha$	$-\alpha$	0	$+\alpha$
V_{ac} (mL) A	40	50	60	40	45	50
V_{dis} (mL) B	800 (fixed)	800 (fixed)	800 (fixed)	800 (fixed)	800 (fixed)	800 (fixed)
m (g) C	0.13	0.45	1.22	0.20	0.35	0.50
V_{melt} (mL) D	NA	NA	NA	20	30	50
m_{NaOH} (g) E	5+5 (fixed)	5+5 (fixed)	5+5 (fixed)	5+5 (fixed)	5+5 (fixed)	5+5 (fixed)
				Fluorspar: 0.20	0.25	0.45
				Cryolite: 0.20	0.24	0.36
				AlF ₃ : 0.12	0.24	0.36
					0.48	0.60
					0.65	0.80
					0.63	0.70
					0.48	0.60
					0.70	0.80

2.4.3.1. Anhydrite

A simple CCD employing twelve experiments ($2^2 + 2 * 2 + 4$) was applied in anhydrite samples to achieve the optimal values for fluorine recovery.

The volume of acid and sample amount were the significant variables studied. The lowest level of volume of acid (20 mL) was reconsidered and set at 40 mL to avoid problems related to overheating of the distillation system, as was previously observed in the screening phase.

2.4.3.1. Fluorspar and fluoroaluminate compounds

A fractional factorial design (Resolution III) was applied using twelve experiments ($2^{3-1} + 2 * 3 + 2$) where one variable was combined with the others in a balanced way.

Fluorspar. A fractional factorial of CCD was built considering the variable with the highest p-value obtained in the screening phase as a variable

confounded with two-variable interaction. The volume of acid (A) was chosen as a combination of the others: sample amount (C) and melt solution (D). *Fluoroaluminate compounds*. For these materials, the volume of melt (D) was included in the CCD and defined as a combination of the other main variables: volume of sulfuric acid (A) and sample amount (C).

2.5 Validation of the models' prediction

The optimal conditions obtained were performed experimentally by applying the predicted conditions. Three samples of each material were analyzed in triplicate to validate the prediction of the models. Fluorine recovery values were calculated as: $F (\%) \pm t \cdot s / \sqrt{N}$ at a 95 % confidence level. Values in fluorspar were expressed as CaF₂ (%).

For evaluating the reliability of results, accuracy and precision were calculated and expressed as relative error RE (%) and relative standard deviation, RSD (%).

Calibration curves were obtained at a potential value defined by: $E (v) = (84.0 \pm 0.1) - (-58.4 \pm 0.2) \log [F]$ for anhydrite; $E (v) = (87.2 \pm 0.2) - (58.1 \pm 0.4) \log [F]$ for fluorspar, $E (v) = (84.3 \pm 0.2) + (-59.0 \pm 0.2) \log [F]$ for cryolite and $E (v) = (94.0 \pm 0.7) + (-60.0 \pm 0.4) \log [F]$ for aluminium fluoride samples with a R² higher than 0.9998 in all cases.

3 Results

3.1 Screening phase

3.1.1. Anhydrite

Results obtained in the screening phase are summarized in **Table 4**. The volume of distillate (V_{des}) and the interaction (volume of acid and volume of distillate) had a significant effect (p-value < 0.05). Even if the volume of acid did not show to be significant itself, its interaction did. Then, it was included in the optimization phase since it played an important role during the distillation process as it was observed throughout the experimental performance.

Table 4. a) Significance (p values) of variables and b) their interactions studied in the optimization procedure with a screening design for anhydrite (full factorial design), fluorspar and cryolite (fractionated factorial design). The significant values (p < 0.05) are in bold, and the effect in parenthesis. Model suitability expressed as R². (NS: No significative. NA Not applicable.).

Variable	V _{ac} (mL)	V _{des} (mL)	m (g)	V _{melt} (mL)	m _{NaOH} (g)	R ²
	A	B	C	D	E	
Anhydrite	0.7853 (NS)	0.0017 (+)	0.0136 (--)	NA	NA	0.98
Fluorspar	0.0221 (-)	NA	0.0170 (--)	0.0032 (--)	NA	0.9998
Cryolite	0.0024 (-)	NA	0.0011 (--)	NA	NS	0.9650
a) Effects	A*B	A*C	B*C	A*D	C*D	D*E
Anhydrite	0.0466 (-)	0.2333 (NS)	0.2254 (NS)	NA	NA	NA
Fluorspar	NA	N.A.	NA	NA	NA	NA
Cryolite	NA	0.0053 (-)	NA	NA	NA	NS

Regarding the opposite signs of the volume of distillate and anhydrite mass, it makes sense to extract a higher fluorine amount by employing a higher volume of distillate, and less sample amount promotes yielding more efficient fluorine extraction during distillation.

Even if the volume of distilled effect was not negligible, it was finally decided to fix it at 800 mL as in the reference method for subsequent experiments and ensure maximum fluorine extraction, indeed.

3.1.2. Fluorspar and Fluoroaluminate compounds

In fluorspar samples, the three variables significantly influenced the response and were inversely proportional to the response regarding the negative value of the coefficients. This means that the yield of the extraction is more effective when less amount of mass is used. The significance of variables and their interactions are gathered in **Table 4**.

These findings were coherent by the fact that less amount of sample led to a total dissolution of the sample, and then less volume of melt solution is

required to accomplish the extraction of fluorine during the distillation. This fact leads to a higher availability of free sulfuric acid in the distillator to extract fluorine from the matrix, increasing fluorine recovery in the distillate.

Considering cryolite samples, similar results were obtained as in the latter case regarding the volume of acid and sample amount effects however, NaOH amount was not a significant variable (p -value > 0.05). Thus, it was considered to study the effect of volume of melt in the sample pretreatment of fluoroaluminate compounds for the optimization phase of these compounds,

3.2 Optimization phase

The significance of variables and their interactions p -values are compiled in **Table 5** for each of the fluorinated samples studied.

Table 5. a) Significance (p values) of variables and b) their interactions obtained in the optimization procedure with a CCD for anhydrite (full factorial design), fluorspar and fluoroaluminate compounds (fractionated factorial design). The significant values ($p < 0.05$) are in bold, and the effect in parenthesis. Model suitability expressed as R^2 . (NS: No significant. NA: Not applicable.).

a)	Variable	V_{ac} (mL)				m (g)				V_{melt} (mL)				R^2
		A	C	D		A	C	D		A	C	D		
	Anhydrite	NS	0.0001	NA	0.0001	NS	NS	NS	0.0003	NS	NS	NS	95.0	
	Fluorspar	NS	(-)	0.0788	NS	NS	NS	NS	NS	NS	NS	NS	92.0	
	Cryolite	0.0061	0.0158	NS	0.0158	(-)	NS	NS	0.0175	0.0478	NS	NS	95.7	
	Aluminium fluoride	NS	0.0473	NS	0.0473	(-)	NS	NS	NS	NS	NS	NS	97.0	
b)	Effects	A*C	A*D	C*D	A*A	C*C	D*D							
	Anhydrite	NS	NA	NA	0.0003	NS	NA							
	Fluorspar	0.0761	NS	NS	NS	NS	NS							
	Cryolite	0.0415	0.0285	0.0102	0.0175	0.0478	0.0425							
	Aluminium fluoride	NS	NS	NS	NS	NS	NS							

3.2.1. Anhydrite

According to the results, sample amount was the only significant variable as well as its interaction. Likewise, the prediction of the model was only governed by the quadratic term, being a two-dimensional response plot enough to evaluate the affecting sense of the model, **Fig. 1a**.

The model predicted a maximum response with 0.13 g sample and 60 mL of sulfuric acid to perform the distillation process.

3.2.2. Fluorspar and fluoroaluminate compounds

3.2.2.1. Fluorspar

Different response surfaces were obtained and plotted in **Fig. 1 b,c,d**.

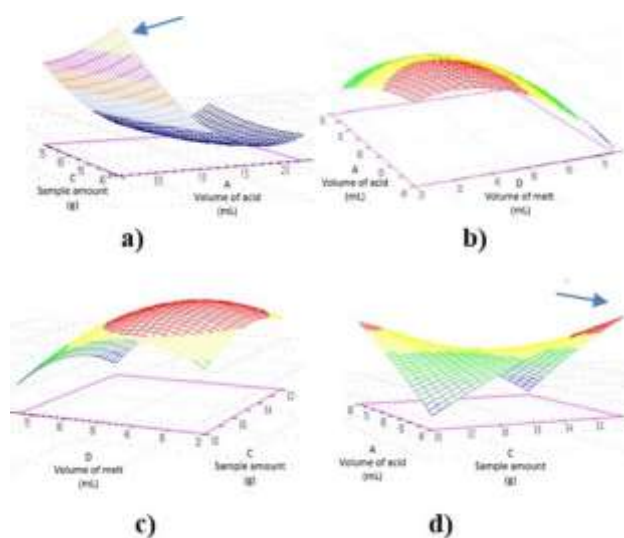


Figure 1. Response surfaces obtained after MLR regression in the sample treatment optimization design (CCD) corresponding to anhydrite **a)** and fluorspar **b,c,d)** samples. Predicted conditions and responses' value (y_{pred}) were anhydrite **a)** m 0.130 g, V_{ac} 42 mL, Y_{pred} 3.44 % F, **b)** V_{melt} 30 mL, V_{ac} 40 mL, y_{pred} 96.7 %CaF₂, **c)** m 0.4750 g, V_{melt} 40 mL, y_{pred} 93.5 %CaF₂ and **d)** m 0.8g, V_{ac} 80 mL y_{pred} 109.0 %CaF₂ and m 0.2g, V_{ac} 40 mL, y_{pred} 116.4 % CaF₂.

Several maximum points of the response appear in the prediction curve. Among them, the optimal conditions predicted in **Fig. 1c)** were discarded since the predicted response (93.5%) was lower than the reference value (97.1%). The rest of the experimental conditions according to the prediction models were assayed without any satisfactory results. Lower values of fluorine recovery than those predicted by the model and by the reference methodology were obtained.

Despite the prediction models failing, conditions of the optimal point indicated in **Fig. 1d)** were selected

(m 0.2g, V_{ac} 40 mL), but increasing the volume of acid at 60 mL (instead of 40 mL). This consideration was established taking into account the following reasons: i) an increase of the volume of acid may extract a higher amount of fluoride from the matrix as it was observed in the screening phase and ii) it was experimentally verified that when the $V_{ac}:V_{melt}$ ratio increased, the free acid is higher which enhances fluoride extraction. Reconsidering these aspects, it was obtained that 20 mL melt solution containing 0.2 g of sample followed by distillation employing 60 mL of acid were the optimal values of the variables that yield comparable results to the values of the reference methodology.

3.2.2.2. Fluoroaluminate compounds

Cryolite. Based on the results, the amount of cryolite and volume of sulfuric acid were the most significant variables followed by their interactions (**Table 5**). Response surfaces were plotted to find the optimum predicted by the model, **Fig. 2a,b,c**.

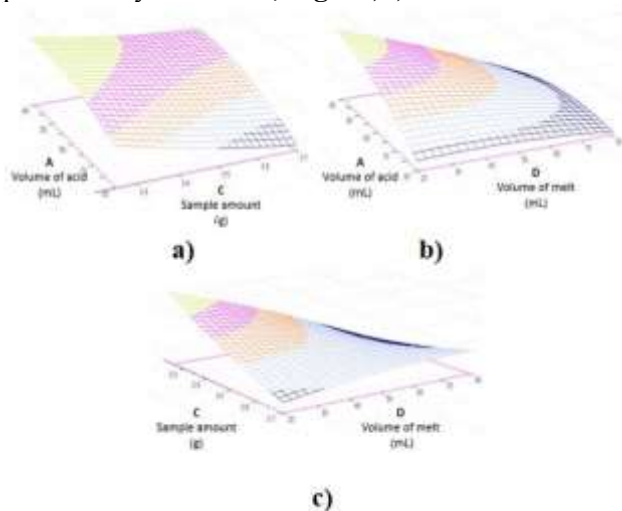


Figure 2. Response surface obtained after MLR regression in the optimization design (CCD) corresponding to cryolite samples. Predicted conditions and responses' values (y_{pred}) were **a)** m 0.25g, V_{ac} 40 mL, y_{pred} 52.78 % F; **b)** V_{ac} 40 mL, V_{melt} 20 mL, y_{pred} 55.63% F and **c)** m 0.25 g, V_{melt} 20 mL, y_{pred} 55.63 % F.

According to the response plots, 0.25 g cryolite, 20 mL volume of melt and 40 mL of acid were the predicted variables to achieve maximum fluorine recovery.

Aluminium fluoride. Attending to the significant variables test, the mass of aluminium fluoride was the only significant variable that explained the model prediction for the fluorine extraction, **Table 5**. Likewise, and according to the graphical depictions

of the response surfaces plotted in **Fig. 3a,b,c**, 0.3 g aluminium fluoride and 20 mL volume of melt to distillate by using 40 mL of acid were the optimal conditions predicted by the model.

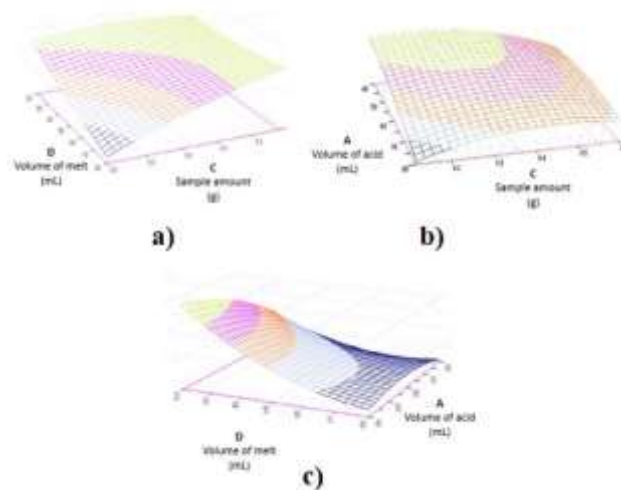


Figure 3. Response surfaces obtained after MLR regression in the optimization design (CCD) corresponding to aluminium fluoride samples. Predicted conditions and responses' values (y_{pred}) were **a)** m 0.25 g, V_{melt} 20 mL, y_{pred} 61.98% F **b)** m 0.25g, V_{ac} 40 mL, y_{pred} 62.36%; and **c)** V_{ac} 40 mL, V_{melt} 20 mL, y_{pred} 62.56 %F.

3.3. Validation of the models' prediction

The optimal conditions predicted for each model were applied for the analysis of three samples of the targeted materials produced in industrial processes. The obtained results compared to those predicted by the optimization performed and the reference values obtained by the DDF reference methodology are summarized in **Table 6**.

Table 6. Predicted values obtained from the curve response of anhydrite, fluorspar, cryolite and aluminium fluoride samples; compared to the experimental values and those obtained by the reference methodology. Values were calculated as: $x (\%) \pm t*s/\sqrt{N}$ at 95 % confidence level). Fluoride content was expressed as F (%) except for fluorspar (CaF_2 (%)).

Compound	Predicted (% F)	Experimental (% F)	DDF Reference (% F)	RE (%)	RSD (%)
Anhydrite					
A_1	3.44	3.3 ± 0.2	3.2 ± 0.1	3.125	6
A_2		1.3 ± 0.4	1.4 ± 0.2	7	31
A_3		0.58 ± 0.09	0.63 ± 0.08	8	16
Fluorspar					
F_1		96.0 ± 0.2	97 ± 1	1	0.2
F_2	116.4	95.4 ± 0.7	96.5 ± 0.5	1	0.7
F_3		97.2 ± 0.3	97.1 ± 0.4	0.1	0.3
Cryolite					
C_1		51.65 ± 0.07	51.6 ± 0.3	0.1	0.1
C_2	55.63	53.0 ± 0.1	53.2 ± 0.5	0.4	0.2
C_3		53.9 ± 0.8	52.9 ± 0.4	2	1
AlF₃					
Al_1		61.4 ± 0.3	61.54 ± 0.02	0.2	0.5
Al_2	62.56	62.0 ± 0.4	61.3 ± 0.6	1	0.6
Al_3		60.4 ± 0.5	60.9 ± 0.2	0.8	0.8

Based on the results, extraction of fluorine by distillation with sulfuric acid suggests satisfactory recovery values of fluorine under the optimized experimental conditions performed. Results agree within the confidence interval compared to the DDF reference values. Except for anhydrite materials, accuracy and precision obtained were very good and less than 1.0 % and 0.8 %, respectively. Higher values were obtained for anhydrite samples (RE 8 % and RSD 31 %) whose fluorine content is less than in the other target materials. This implies higher values of RE and RSD for lower percentages of fluorine, being the precision the most affected by the application of the methodology at low fluorine content.

4 Discussion

Optimized methodology

In general, fewer sample amounts were required in the optimized conditions than in the reference methods, in agreement with the negative signal effect of this variable obtained along the DoE performed. Fluorspar and fluoroaluminates ratio values (volume of acid/volume of melt) were triple and double respectively compared to the ratio in the reference methods (1.5). This observation could be related to the strength of the acids to extract fluorine from the

matrix, indicating that a greater volume of sulfuric acid is required to balance this aspect compared to the strength of the perchloric/phosphoric acids mixture.

Likewise, fluorspar samples demanded more volume of melt to distillate compared to the fluoroaluminates, which could be explained due to their physical-chemical properties. More severe conditions were required to overcome the forces that hold the lattice between Ca-F. In fact, fluorspar is the compound with higher lattice energy regarding to the melting point series among the target compounds $\text{CaF}_2 > \text{AlF}_3 > \text{cryolite}$ [31]. Moreover, the high purity level of fluorspar samples (>90%) compared to the fluoroaluminate ones (50-65%) has to be additionally considered.

Comparative with ISO norms

The optimized methodologies of fluoroaluminate derivatives require less volume of acid than ISO standard norms [23,24]: 40 mL sulfuric acid in the optimized procedure compared to 50 mL sulfuric acid in ISO standards. In the case of fluorspar, distillation is achieved using more volume of acid (60 mL sulfuric acid) than in the ISO standard norm [22], in which 35 mL of perchloric acid is employed. However, costs, safety and environmental benefits are balanced in this latter case.

Another aspect to consider concerning ISO norms is the method to determine fluorine compared to the method used in this study by F-ISE potentiometry. Considering the determination of fluorine in ISO norms, titration with LaNO_3 (fluorspar) or with $\text{Th(NO}_3)_4$ (fluoroaluminate derivatives) is performed, which is not in agreement with the practice of green analysis by reducing or avoiding harmful reactants, even more in the case of handling thorium due to its radioactive characteristics.

Costs, environmental and safety benefits

The optimized experimental conditions reduce not only the volume of acid but also the amount of sodium hydroxide, which represents a saving in the consumption of reagents and a reduction in the volume of waste compared to the reference method. In fact, a saving of up to more than 20% per liter is achieved using sulfuric acid instead of perchloric acid according to the market price. On the other hand, the optimized procedure avoids the use of perchloric acid which is potentially dangerous due to the risk of explosion that involves its manipulation and treatment of chlorinated wastes, greening the analysis for routine purposes [32,33].

Applicability

This optimized approach may be applied not only for the quality control of raw materials and intermediate products in the HF industry but also, for the analysis of by-products from fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) used in fertilizers manufacturers or by-products from the electrolysis of cryolite in the smelting process. Furthermore, the importance of quality control is crucial in these fluorine-containing materials, as it allows timely adjustments of the parameters of the HF manufacturing process and, therefore, adequate compliance with product specifications.

Environmental labs require as well analytical approaches for the assessment of fluorine distribution in wastes from landfills and in fluorine-contaminated soils near storage sites from industry [19].

In addition, these methodologies allow ensuring the implementation of new instrumental techniques, and even as an alternative methodology in situations where instrumental failures may occur.

5 Conclusion

The chemometric approach for the optimization of the fluorine separation procedure of fluorinated target compounds has been demonstrated in terms of experimental design. Results from factorial designs showed that the amount of sample and volume of acid were the most influential parameters on fluorine extraction.

Fluorine values obtained by ISE-potentiometry agreed with those obtained by the reference method. Thus, the modifications of the optimized conditions for the sample pretreatment allowed the substitution of the perchloric/phosphoric acids mixture by employing sulfuric acid. The implementation of the new optimized conditions ensures economic and occupational exposure benefits in agreement with the principles of the laboratories' quality control systems, including a reduction of wastes in conformity with the actual consensus for more greening procedures of analysis.

These alternative approaches may be applied to those fluorine-containing materials that require fluorine extraction and analysis for: quality purposes, fluorine environmental assessment in soils and industrial wastes, and HF manufacturing process control which depends on fluorine content analysis to monitoring reactors' parameters.

More investments are needed in research for the development and acquisition of new

instrumentation for the analysis of fluorine to obtain fast and reliable results in fluorine-containing materials, whose chemical complexity makes them a great challenge for the development of new analytical methods.

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