Ion chromatography applications in the determination of HF, HCl, NO_x, SO_x on stationary emissions

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Summary. - In this work, specific topics will be covered in order to verify an effective, routine application of ion chromatography as a suitable and approved technique for emission monitoring in the determination of HF, HCl, NO_X and SO_X on stationary emission. A review of the analytical methods as proposed by recent updates in Italian environmental law and the problems encountered in the application of this method, such us the interference due to high level of carbonate, high hydroxides concentration particularly on SO_X and NO_X absorbing solution, are considered in the present work. The sample treatments before the IC analysis, this to reduce the matrix interference due to the strong basic solutions used to monitor different stationary emissions, are also examined. Some modifications in sampling are explored to find more suitable conditions for the IC analysis.

Key words: ion chromatography, absorbing solutions, sampling method.

Riassunto (Applicazioni della cromatografia ionica nella determinazione di HF, HCl, NO_x , SO_x nelle emissioni stazionarie). - In questo lavoro, sono trattati specifici argomenti allo scopo di valutare l'utilizzo della IC come tecnica semplice e di affidabile applicazione per il monitoraggio delle emissioni. Sono stati presi in esame i metodi analitici proposti dall'attuale legge ambientale italiana; la verifica dei problemi riscontrati nell'applicazione degli stessi, quali le interferenze dovute all'elevato contenuto di carbonati, l'elevata concentrazione di idrossidi in particolare nelle soluzioni di assorbimento per SO_X e NO_X ha portato a valutare condizioni analitiche diverse da quelle indicate nei metodi ufficiali. Sono state individuate alcune modifiche da apportare in fase di campionamento allo scopo di facilitare l'analisi cromatografica degli assorbimenti. Viene inoltre presa in considerazione la fase di preparazione del campione prima dell'analisi IC allo scopo di minimizzare le possibili interferenze dovute alla forte alcalinità delle soluzioni di assorbimento utilizzate nel campionamento delle emissioni.

Parole chiave: cromatografia ionica, soluzione assorbente, metodo di campionamento.

Introduction

Recent updates in Italian environmental Law relative to the use of sampling methods, analysis and macro-pollutant evaluation on stationary emissions, have led to a requirement for improvements in ion chromatography (IC) analysis [1-6].

The development of these methods using different basic absorption solutions allow the quantification of contaminants such as SO_X , NO_X , HCl, HF to be performed with ion chromatography using suppressed conductivity detection.

These sampling methods are described in detail in the protocols enclosed in the Italian Law, while the optimisation of the analytical procedures is left to the different laboratories performing IC analysis [7, 8].

A new method for the determination of HCl, HF, NO_X , SO_X in strong basic absorption solutions was developed to enable rapid analysis, taking into account the limitations of presently available instrument accuracy and sensitivity [9, 10].

However some problems occur at low concentration ranges that could cause a loss of accuracy in the quantification of these pollutants.

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In this work we will describe the problems encountered due to the high pH of the absorbing solution, the possible contamination arising from sample pre-treatments and interference of different matrices. Furthermore, we will consider the advantages and disadvantages of two different chromatographic approaches based on the use of carbonate and hydroxide selective columns, and also the availability of sampling solutions more suitable absorbing for ion chromatography purposes. Our laboratory performs the emission samplings and analytical checks on stationary emission sources these include various production processes, such as electrical power generation plants, elastomer production centres and hazardous waste incineration plants; therefore the samples that we analyse have different origins and contain varying levels of pollutants.

Experimental

Equipment

The high-performance liquid chromatography systems used in this study consisted of: (a) Dionex DX100[®] ion chromatography (Sunnyvale, CA, USA) equipped with an AS40[®] autosampler (Dionex, Sunnyvale, CA, USA); (b) Dionex DX600[®] ion chromatography (Sunnyvale, CA, USA) equipped with an AS50[®] autosampler (Dionex, Sunnyvale, CA, USA), and an EG40[®] eluent generator (Dionex, Sunyvale, CA, USA).

System (a) was used with an IonPac[®] AG9HC guard column (4 x 50 mm) (Dionex, Sunnyvale, CA, USA) in combination with an IonPac[®] AS9HC analytical column (4 x 250 mm) (Dionex, Sunnyvale, CA, USA). Isocratic elution (1 ml/min) were performed: *SETUP A*, with 9.0 mM Na₂CO₃; *SETUP C*, with 8.0 mM Na₂CO₃ and 1.5 mM NaOH.

System (b) was used with an IonPac[®] AS15-5 μ m analytical column (3 x 150 mm) (Dionex, Sunnyvale, CA, USA) and an IonPac[®] AG15-5 μ m guard column (3 x 30 mm) (Dionex, Sunnyvale, CA, USA). Elution (0.5 ml/min) was isocratic 10 mM KOH during 0-4 min, and a combination of linear gradients 10-60 mM KOH during 7 min, 60-40 mM KOH during 3 min, and 40-60 mM KOH during 26 min, *SETUP B*.

The analytes were detected by suppressed conductivity using an ASRS Ultra[®] anion self-regenerating suppressor (Dionex, Sunyvale, CA, USA) and the data was processed using Chromeleon[®] 6.2 IC software (Dionex, Sunnyvale, CA, USA).

Chemicals

All chemicals used in this study were of analytical grade purity, Na₂CO₃, KNO₃, Na₂SO₄, NaCl and NaF were supplied by BDH (Poole, Dorset, BH15, ITD,

UK), NaOH by Baker (Deventer, Holland) and KMnO₄ and H_2O_2 by Carlo Erba (Milano, Italy), ultrapure water Milli-Q Plus System[®] 18.2 M Ω x cm a 25 °C (Millipore, MA, USA)

Determination of SO_X and NO_X

The sampling procedure of SO_X , NO_X is based on sulphur and nitrogen oxides absorption obtained from the bubbling process of a gaseous flow through an alkaline potassium permanganate solution (0.025 M KMnO₄ in 1.25 M NaOH) [9-13].

The sampling train is set up filling each of the bubblers with 30 ml of absorption solution and preparing the drying tower using column with silica gel. The sampling is performed for 1 hour at a sampling rate of 0.3 l/min. Fig. 1 shows a scheme of the sampling train.

The oxidation products, sulphates and nitrates, were determined by IC after the reduction of the permanganate with hydrogen peroxide (30% m/m, H_2O_2) as shown below.

 $2 \text{ MnO}_4^- + 3 \text{ SO}_3^{2^-} + \text{H}_2\text{O}_2 \Leftrightarrow 3 \text{ SO4}^{2^-} + 2 > \text{MnO}_2 + 2 \text{ OH}^ 2 \text{ MnO}_4^- + 3 \text{ NO}_2^- + \text{H}_2\text{O}_2 \Leftrightarrow 3 \text{ NO}_3^- + 2 > \text{MnO}_2 + 2 \text{ OH}^-$

Analytical procedure. - The contents of both the first and the second bubblers and rinsing waters of the sampling train are transferred into a 100 ml volumetric flask (solution A). The contents of the third bubbler, and its rinsing water are transferred into a 50 ml volumetric flask (solution B).

To aid the reaction the H_2O_2 is dipped directly into the stirred solution. When the reaction is complete a precipitate of manganese dioxide will be present in the bottom of the flask.

If the solution remains lightly coloured, yellowbrown, it is necessary to stir until the precipitation is complete and the solution is colourless.

The excess of H_2O_2 has to be eliminated before injection into the ion chromatograph. This is achieved by stirring or lightly heating the solution until the generation of oxygen has finished allowing the precipitate to settle.

Determination of HF and HCl

The analytical determination of hydrochloric and hydrofluoric acids for different stationary emissions is based on the absorption in the alkaline solution of sodium hydroxide (0.1 M NaOH) followed by IC analysis [13, 14]. Fig. 1 shows a scheme of the sampling train.

The sample of gas, including gaseous and aerosol parts, was absorbed in the bubblers. A quartz wool filter was used in order to block any dust present in the gas; this filter is placed down stream of the nozzle in



Fig. 1. - Sampling train scheme.



Fig. 2. - Matrix interference due to the carbonates. Chromatographic conditions: Dionex DX100[®] ion chromatography, IonPac[®] AG9HC guard column (4 x 50 mm), IonPac[®] AS9HC analytical column (4 x 250 mm), eluent 9.0 mM Na₂CO₃, isocratic elution (1 ml/min).

the stack. The suction tube was made of glass and downstream a cooler is attached. The absorbent solution is linked to the condenser; inside the bubblers a precise quantity (30 ml) of the specific absorption solution and is used as a liquid absorber. The sample gas is cooled down to below 0 $^{\circ}$ C.

The sampling is carried out at a range of temperatures between $120 \text{ }^{\circ}\text{C}$ - $130 \text{ }^{\circ}\text{C}$ for 1 hour at a sampling rate of 0.5 l/min.

Analytical procedure. - The contents of the first and second bubblers and the rinsing waters of the sampling train are transferred into a 100 ml volumetric flask (solution A), the content of the third bubbler and its rinsing water is transferred into a 50 ml volumetric flask (solution B).

Both methods are applicable in different concentration ranges varying the alkalinity of the absorption liquid used.

Discussion

The requirements indicated by Italian law for the use of ion chromatography in the determination of these parameters necessitated the choice of a high capacity column with carbonate eluent to perform the analysis of HCl, HF, NO_X , SO_X .

Different analytical conditions were evaluated in order to find a uniform protocol suitable for encompassing all these determinations.

The peculiarity of the sampling methods, the high alkalinity absorption solutions and the preparation procedure of the samples, necessitated the use of a specific H^+ resin cartridge (OnGuard[®] H Dionex) to reduce the concentration of hydroxides before the injections [6].

In these conditions, the check of the blanks, absorption solutions, pre-treatment cartridges etc. became very important. This was to ensure the accuracy of the analytical data within the requirements of the different plants emissions to check for possible interference due to the sulphates released from the cartridge itself. The different emissions monitored, such as waste and hazardous incinerator, elastomer production, power generation plant, had shown common matrix interference in the determination of HCl.

The presence of carbonate can induce severe modifications to the shape of the chromatographic peak. This can be seen on the leading edge of the chlorine and may cause difficulties with quantification (Fig. 2).

In the application of the method, (*SETUP A*), for the quantification of SO_X and NO_X on electrical power generation plants, using oil with a medium sulphur content (less than 1%) as fuel, an additional possible interference was found. This was related to the high alkalinity of the absorption solutions during the analysis of emission samples, and therefore the concentration of sulphate could be under-estimated [10]. This was attributed to an overload of the suppressor caused by the strong basic solutions injected (Fig. 3). Dilutions of the same samples produced sulphate peaks previously not detectable (Fig. 4).

The difficulties encountered in the application of a common protocol for the determination of HCl, HF, NO_X , SO_X led to development of a new analytical



Fig. 3. - Matrix interference due to the high alkalinity of the absorption solution. Chromatographic conditions: Dionex DX100[®] ion chromatography, IonPac[®] AG9HC guard column (4 x 50 mm), IonPac[®] AS9HC analytical column (4 x 250 mm), eluent 9.0 mM Na₂CO₃, isocratic elution (1 ml/min).



Fig. 4. - Effect due to the sample dilutions.



Fig. 5. - Analytical response of carbonate (dotted line) and sulphate in a hydroxide selective column. Chromatographic conditions: Dionex DX600[®] ion chromatography, lonPac[®] AG15-5 μ m guard column (3 x 30 mm), lonPac[®] AS15-5 μ m analytical column (3 x 150 mm), injection volume 25 μ l, isocratic elution (0.5 ml/min).

Time (min) and concentration (mM) KOH in parenthesis: 0:00 (10); 4:00 (10); 11:00 (60); 14:00 (40); 30:00 (60).



Fig. 6. - Chromatogram relative to the differente composition of the eluent. Chromatographic conditions: Dionex DX100[®] ion chromatography, IonPac[®] AG9HC guard column (4 x 50 mm), IonPac[®] AS9HC analytical column (4 x 250 mm), eluent 8.0 mM Na₂CO₃ and 1.5 mM NaOH, isocratic elution (1 ml/min).

procedure. A first step in this optimisation was the choice of a different IC column; an hydroxide selective column (Dionex Ion Pac[®] AS15) was tested (*SETUP B*).

As shown in the chromatogram (Fig. 5) the carbonate and the sulphate have similar retention times therefore these analytical conditions are not suitable for the determination of SO_X and NO_X .

A solution to the problem, to evaluate all the required analytes with the same protocol, was found by varying the eluent composition and using an Ion Pac[®] AS9HC analytical column. To perform the IC analysis of SO_x and NO_x with this specific carbonate column, the eluent 8.0 mM Na₂CO₃, 1.5 mM NaOH (*SETUP C*) was used instead of the standard eluent 9.0 mM Na₂CO₃ (*SETUP A*) therefore the interference on the chloride peak was eliminated (Fig. 6).

	Absorbing	g solution	Absorbing solution			
	KMNO ₄ 0.025 M	in NaOH 1.25 M	H ₂ O ₂ 30% m/m			
Sample n.	NO _X	SO _X	NO _X	SO _X		
	(mg/m³)	(mg/m³)	(mg/m³)	(mg/m³)		
1	345	765	45	851		
2	295	698	49	748		
	Absorbin	g solution	Absorbing solution			
	KMNO ₄ 0.025 M	I in NaOH 1.25 M	H ₂ O ₂ 30% m/m in NaOH 0.1 M			
Sample n.	NO _x	SO _x	NO _X	SO _X		
	(mg/m³)	(mg/m³)	(mg/m³)	(mg/m³)		
3	349	1141	55	1436		
4	298	1098	53	1213		
	Absorbin	g solution	Absorbing solution			
	KMNO ₄ 0.025 M	l in NaOH 1.25 M	KMNO ₄ 0.025 M in NaOH 0.1 M			
Sample n.	NO _x	SO _X	NO _X	SOx		
	(mg/m³)	(mg/m³)	(mg/m³)	(mg/m³)		
5	228	799	220	645		
6	147	446	202	437		
7	133	288	241	505		
8	85	310	201	439		
9	98	446	152	458		

Table 1.	- Comparison	data of	SOx	and NO _x	between	official	method	and	method	"modified
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The best injection volume seems to be $20 \,\mu$ l, a good compromise between the OH⁻ injected and the sensitivity requested.

In this way it was possible to perform the analysis of HCl, HF, NO_X , SO_X , with the same column in a single IC run.

Conclusions

Different NO_X, SO_X sample solutions were tested in order to improve both sampling and analytical conditions reported in the official method. The composition variation of the absorption solutions could improve the IC analysis compatibility. The high alkalinity of the absorption solutions is the main problem for anion exchange analysis so a dilution of the sample before the injection is always recommended. Three different alternative sample solutions were tested: hydrogen peroxide (30% m/m H_2O_2), hydrogen peroxide (30% m/m) in 0.1 M NaOH, and a solution of 0.025 M potassium permanganate in 0.1 M sodium hydroxide were tested. The comparison data obtained for SO_X and NO_X are shown in Table1. The experiences in testing various emission sources have shown that further improvements have to be carried out in order to optimise these IC methods and allow an easy and uniform approach suitable for encompassing all these types of emissions.

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