

ANALYSIS OF HBR, HCL AND SO₂ PRODUCED DURING THERMAL DEGRADATION OF MATERIALS

ADAPTATION OF A STANDARDIZED METHOD

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Abstract

La norme NF X 70-100 (Avril 2006) définit les méthodes à utiliser pour analyser les effluents de combustion des matériaux. Elle prévoit notamment de piéger HBr et HCl dans de l'eau sous forme d'ions Cl⁻ et Br⁻ puis de les doser par titrage potentiométrique avec électrode d'argent ou par Chromatographie Liquide Ionique (C.L.I.). De même, SO₂ est piégé sous forme SO₄²⁻ dans un mélange d'eau et d'eau oxygénée, puis dosé par C.L.I.. Enfin, lors de l'essai, les quantités de CO et de CO₂ sont mesurées en continu à l'aide d'analyseurs à Infra-Rouge Non Dispersif. Ces méthodes a priori incompatibles nécessitent donc autant de groupes séparés de combustion pour doser chacun des gaz précités.

L'objectif du travail réalisé est de développer la méthode permettant de piéger simultanément HCl, HBr et SO₂ dans le même milieu de piégeage (H₂O + H₂O₂), puis de doser les trois espèces correspondantes par C.L.I., tout en autorisant le dosage en cours de combustion de CO et CO₂. La validation de cette nouvelle méthode comprend les étapes suivantes : vérification de la non influence du milieu de piégeage sur le dosage de CO et CO₂, vérification de la sélectivité, de l'absence d'influence de la technique de dosage, étude de la linéarité, calcul des limites de détection et de quantification. Les incertitudes ont également été estimées.

Comparée à la méthode précédemment utilisée par le laboratoire, la C.L.I. associée au piégeage dans H₂O + H₂O₂ améliore l'exactitude des résultats. Les limites de détection et de quantification sont également plus faibles. Pour des analyses en routine réalisées quotidiennement au laboratoire, cette méthode est économiquement très intéressante.

The NF X 70-100 (April 2006) standard defines the methods to be used in order to analyze the effluents of the combustion of materials. It envisages in particular to trap HBr and HCl in water in the form of Cl⁻ and Br⁻ ions and to determine their quantity by titrimetry with silver electrode or Ion Liquid Chromatography (I.L.C.). Likewise, SO₂ is trapped as SO₄²⁻ using a hydrogen peroxide supplemented water, and subsequently quantified using I.L.C. At last, during the test, the quantities of CO and CO₂ are continuously measured using Non-Dispersive Infra-Red analysers. These methods, incompatible at first glance, consequently requires as many separated groups of combustion, in order to quantify each mentioned gas.

The objective of the carried out work is to build up the method, which allows to trap simultaneously HCl, HBr and SO₂ in the same trapping solution (H₂O + H₂O₂), then to determine the quantity of the three corresponding species by I.L.C., as well as allowing the measurement of the quantity of CO and CO₂ during the combustion. The validation of this new method includes the following stages : checking the non influence of the medium of trapping on the measurement of the quantity of CO and CO₂, checking the selectivity, the absence of influence of the measurement technique, of the trapping solution, study of the linearity, calculation of the limits of detection and quantification. Uncertainties were estimated too.

Compared with the method previously used by the laboratory, the I.L.C. associated with the trapping in H₂O + H₂O₂ improves the exactitude of the results and is more relevant economically. The limits of detection and quantification are also weaker.

Scope

One of the services LNE relates to the measurement of the quantities of gas species released during the combustion of materials. The gas list includes the following species: carbon monoxide, carbon dioxide, hydrochloric acid, hydrobromic acid, sulphur dioxide, hydrocyanic acid and hydrofluoric acid.

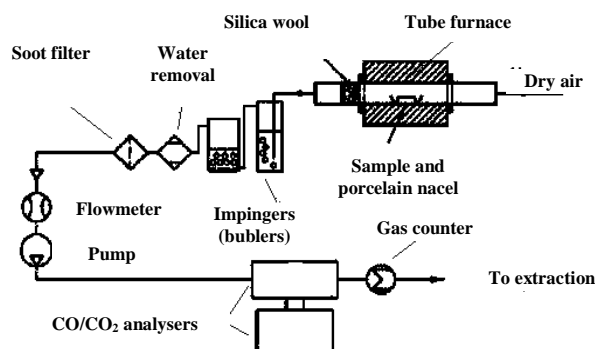
The whole measurement method is detailed in the standard NF X 70-100 of April 2006 [1] [2]. Part 2 of this standard explains the method used for the thermal degradation of materials in a tubular furnace, and when needed, the way to trap the gases to be analysed. Part 1 then details various methods of gas analysis, adapted to the nature of the gases coming from thermal degradation.

As all these gases are extremely toxic for the organism, it is important to measure their quantity. Depending on their nature, they may be analysed continuously through specific light absorption means, or be trapped in a specific solution.

The techniques referred in the standard are presented in the table below:

CO CO ₂	Non Dispersive InfraRed spectrometry (N.D.I.R.)
HBr HCl	Absorption in Water (H ₂ O medium) Cl ⁻ and Br ⁻ measured by AgNO ₃ titrimetry or Ion Liquid Chromatography (I.L.C.) – Conductimetric detector
HCN	Absorption in Sodium hydroxide 0,1 M CN ⁻ measured by spectrophotometry (Sodium picrate method) or Ion Liquid Chromatography (I.L.C.) – Amperometric detector
HF	Absorption in Sodium hydroxide 1 M F ⁻ measured by spectrophotometry (SPADNS method) or Ion Selective Electrode (LaF I.S.E.)
SO ₂	Absorption in Water + Hydrogen peroxide (H ₂ O ₂ medium) SO ₄ ²⁻ measured by Ion Liquid Chromatography (I.L.C.) – Conductimetric detector

The test bench to carry out the materials combustion is shown in the below drawing.



Into a tubular furnace brought up to a temperature of 600 °C is introduced a quartz tube of 1 m length and 40 mm diameter. A pump draws air in the tube furnace at an air flow of 2 l/min. A silica wool filter pad collects the soot released during combustion.

Downstream, right after the quartz tube are the two impingers containing the suitable solution for trapping, depending of the gas to be analysed. The second impinger includes a sintered glass plate that filters the large organic particles and increases the transferring surface between the gas effluents and the trapping solution.

The sample must be weighed very exactly and be introduced into a porcelain boat. The usual mass is 1 gram. If it is impossible to maintain a correct air flow during the test, due to the filling of either the sintered glass plate or the silica wool pad, then the mass of the sample may be lowered to 0,5 g or 0,25 g.

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Lastly, the sample is introduced in the centre of the isothermal part of the tubular furnace with a metallic rod, and let there for the next 20 minutes, then removed. The test is then continued until the effluents of combustion are all flushed from the quartz tube, or 20 more minutes have elapsed. At this point, the test is stopped, and the silica wool pad and the impingers are removed.

After combustion, the silica wool pad is soaked in the suitable trapping solution in order to collect the maximum quantity of analytes (some compounds like HCl are trapped on the soot and water that may condense in the silica wool pad). The whole trapping solution, from the impingers and from the washing of the silica wool pad, is filtered, then poured in a gauged flask, and the volume of trapping solution is completed to the gauge line. The gauged flask usually has a volume of 500 ml, but may have a 1000 ml volume.

After analysis, the amount of gas per gram of material is calculated, using the initial mass of sample, and the volume of the gauged flask.

After the test, the whole tube shall be cleaned by pyrolysis. The total duration of a combustion is thus at least 40 minutes (and up to 60 minutes).

Aims of the project

1) Reduction of the number of analysis

At the present time, approximately 300 series of analysis of toxicity are carried out each year following this standard. They include, per series:

- 3 analysis for CO/CO₂/HCl/HBr with water as a trapping solution for HCl and HBr;
- 1 SO₂ analysis with hydrogen peroxide supplemented water as trapping solution; If SO₂ is found in a measurable amount, then, two more analysis are carried out.
- 1 HCN analysis with 0.1M sodium hydroxide as trapping solution ; If HCN is found in a measurable amount, then two more analysis are carried out.
- 1 HF analysis with 1M sodium hydroxide as trapping solution; If HF is found in a measurable amount, then two more analysis are carried out.

As these four different means are exclusive, it may consequently be necessary to carry out up to 4 series of 3 combustions in order to analyze the 7 aforementioned gases. The aim of this project is then to develop a method allowing to trap HCl, HBr and SO₂ together in the same trapping solution, without disturbing the measurement of the quantity of CO and CO₂ emitted during the combustion, leading thus to 3 sets of 3 combustions instead of 4. This method would allow a saving of time and an increased productivity for all the team.

Hydrogen Peroxide supplemented Water has been found to be a good candidate to achieve this, provided that HCl and HBr are trapped in the same way as they already are in the standard method, and that the measurement of the amount of CO and CO₂ by N.D.I.R. is not disturbed in any way.

2) Improvement of the reliability of the results

2.a) To be free from the lack of accuracy of the titrimetry

- **Proportion between Chloride and Bromide ions**

At the present time, the measurement of the amount of the Cl⁻ and Br⁻ ions in solution is carried out by titrimetry : the electrical potential of the solution is measured by the electrode, and AgNO₃ is progressively added to the solution. As Cl⁻ and Br⁻ ions react with Ag⁺ ions, they precipitate in AgCl and AgBr, which are very poorly soluble in water. The electrical potential of the solution is then affected and, when one of the two compounds is completely precipitated, the electrical potential of the solution suddenly changes, leading to a jump on the curve [AgNO₃] vs Electrical Potential.

When a solution contains Cl⁻ and Br⁻, two jumps of potentials indicate the end of the reaction, the first jump is for the precipitation of AgBr and the second is for the precipitation of AgCl. Both salts have different products of solubility whose ratio is:

$$\frac{(Ks)_{AgBr}}{(Ks)_{AgCl}} = 5 \times 10^{-3}$$

The NF X 70-100 (April 2006) standard, in its appendix F, explains why the co-precipitation of the two halides may involve an inaccuracy on the measurement, depending on their relative proportions.

Two cases may arise:

- If $0.1 \leq [Cl^-]/[Br^-] \leq 5$, the separation is good and the error is less than 5 %.
- If $[Cl^-]/[Br^-] < 0.1$ or $[Cl^-]/[Br^-] > 5$, then the error on the measurement is higher or equal to 10 %². The measurement by titrimetry shall then be carried out through a weighed addition of the minority halide or by another method of analysis.

In Ion Liquid Chromatography, when two ions have a sufficient separation, their relative proportion does not induce any error on the measurement of their respective quantities.

- **Co-precipitation of other ions**

Silver nitrate addition precipitates the Chloride ions and the Bromide ions, but can also precipitate the Fluoride, Iodide ions as well as Cyanide ([Ag(CN)₂]⁻) then [Ag(CN)₂]Ag).

The Ion Liquid Chromatography will make it possible to be freed from the error due to the co-precipitations :

- This technique is more selective than the titrimetry.
- With good chromatographic conditions, the measurement of the quantity of Cl⁻ and Br⁻ ions by I.L.C. will be freed of the error due to their relative proportions

2.b) Improvements of the Limit of Detection

The NF X 70-100 (April 2006) standard gives limits of detection for the Chloride (LD_{Cl}=4 mg/l) and Bromide ions (LD_{Br}=8 mg/l). The Ion Liquid Chromatography is a very sensitive technique which will allow to improve the limits of detection of these ions

2.c) Reduction of the test uncertainties

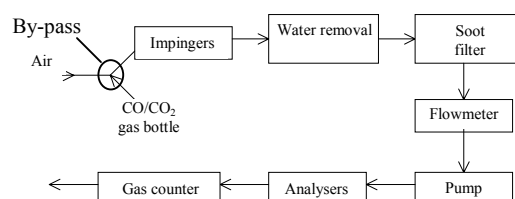
The uncertainty of the result comes from:

- The measurement method, which may be improved due to the inherent qualities of I.L.C. compared to titrimetry.
- The material heterogeneousness, which may be improved by raising the number of combustion, and/or a proper sampling method.

Validation steps

Non-influence of the trapping solution on the measurement of the amount of CO/CO₂

This is achieved through a specific test, made on the standard-defined whole test bench.



A cylinder containing about 5 % of CO and about 20 % of CO₂ in nitrogen (N₂) is connected upstream to the quartz tube. A by-pass allows the dilution of the gas coming from the cylinder with atmospheric air. Thus, several concentrations of CO and CO₂ are available for the measurement, taking the same way as CO and CO₂ emitted by a sample would take in the test bench, up to the analysers.

² These two values - 5 % and 10 % - are not connected, when the conditions of evaluation are. Therefore, they must be taken as indicative values.

Two configurations will be successively compared, at several concentrations:

- Impingers filled with Water (standard defined trapping solution for CO/CO₂/HCl/HBr measurement)
- Same impingers, filled Hydrogen Peroxide supplemented Water (alternate trapping solution)

As the only difference in the test bench is the composition of the trapping solution, any difference between the data obtained with the alternate solution, and the data obtained with the standard defined solution, will then be imputable to the difference of trapping solution.

The measurements are carried out at three different concentrations:

- Full concentration. With a closed by-pass: 5 % CO and 20 % CO₂ (in volume). (The analyses can measure up to 10 % CO and 30 % CO₂, but the standard allows these concentrations to be taken for calibration, for security reasons).
- Average Concentration: 3 % CO and 12 % CO₂ (in volume)
- Weak Concentration: 1 % CO and 4 % CO₂ (in volume)

The two series of concentration measured are then compared, in order to state on the influence of the trapping solution:

- If the two series are statistically considered as equal, then the trapping solution has no influence on the measurement of the amount of CO and CO₂
- If the two series are statistically considered as different, then, the trapping solution has an influence on the result

The results are shown in the table below:

	CO		CO ₂	
	Trapping solution		Trapping solution	
	H ₂ O	H ₂ O + H ₂ O ₂	H ₂ O	H ₂ O + H ₂ O ₂
Low quantity	0.91 %	0.91 %	3.65 %	3.64 %
Intermediate quantity	3.00 %	3.00 %	11.80 %	11.81 %
High quantity	4.54 %	4.54 %	17.38 %	17.38 %

For contents from 0 to 5 % of CO and 0 to 20 % of CO₂, no difference in results is noted. The trapping solution has no influence on the measurement of the amount of CO and CO₂.

Specificity of the method and ILC separation

The measurement conditions are as follow :

Calibration range :

	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6
[SO ₄ ²⁻] (mg/l)	1.000	3.006	5.000	10.00	20.00	30.06
[Br ⁻] (mg/l)	1.000	2.009	5.000	10.00	20.00	20.09
[Cl ⁻] (mg/l)	1.000	1.999	5.000	10.00	20.00	19.99

Analytical system used for the study :

- Ion Liquid chromatograph type Dionex DX500;
- Ion exchange column AS14 (silica grafted with quaternary ammonium functional groups) and pre-column AG14;
- Suppressor type ASRS Ultra 4 mm;
- Detector ED40 (used in conductimetric mode);
- Mobile phase : solution of 3,5 mmol/l Na₂CO₃ and 1 mmol/l NaHCO₃;
- Flow rate of the mobile phase: 1,5 ml/min;
- Autosampler with injection loop of 50 µl;
- Organic filtration (Varian JR-C18 500mg) and mechanical filtration (PTFE 0.2 µm) of samples.

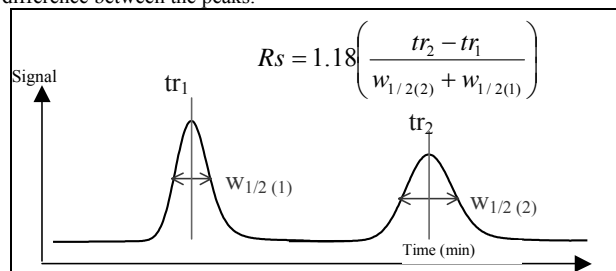
The analyses can be carried out on another type of equipment, with another eluent or a different flow rate, provided that the separation is good enough to allow a quantitative analysis of the studied elements.

Quality of separation

In order to have a matrix representative of the solutions to be analyzed, the combustion of a material is carried out. This material has been chosen as exempt from Chloride and Bromide ions. This has been controlled through a proper titrimetry. 1 ml of this solution, further called combustion matrix, is mixed with 1 ml of a standard poly-anion solution containing: F⁻ (10 mg/l), Cl⁻ (20 mg/l), NO₂⁻ (20 mg/l), Br⁻ (20 mg/l), NO₃⁻ (20 mg/l), PO₄³⁻ (20 mg/l) and SO₄²⁻ (30 mg/l). The analyzed ions are Fluoride, Chloride, Nitrite, Bromide, Nitrate, Phosphate, Sulphate and Acetate.

Study of the quality of separation

This is achieved through the calculation of the resolution. This parameter allows us to consider the quality of separation between two peaks because its calculation takes into account the width at middle height as well as the difference between the peaks.



The resolution for each set of two consecutive peaks has been calculated:

- If the resolution is higher than or equal to 0,6 then a qualitative analysis is possible.
- If the resolution is higher than or equal to 1,5 (return to the base line), then a quantitative analysis is possible.

Ion	Retention time (min)	Width at middle height (min)
F ⁻	2.33	0.07
Acetate	2.57	0.16
Cl ⁻	3.27	0.09
NO ₂ ⁻	3.83	0.11
Br ⁻	4.73	0.14
NO ₃ ⁻	5.49	0.17
HPO ₄ ²⁻	7.12	0.25
SO ₄ ²⁻	8.53	0.27

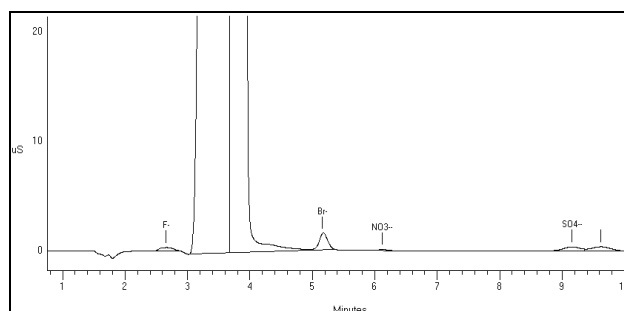
Ion couple	Resolution
F ⁻ / Acetate	1.23
Acetate / Cl ⁻	3.30
Cl ⁻ / NO ₂ ⁻	3.30
NO ₂ ⁻ / Br ⁻	4.25
Br ⁻ / NO ₃ ⁻	2.89
HPO ₄ ²⁻ / SO ₄ ²⁻	3.20

Acetate ions in solution come from the acetic acid used in the washing machine. Traces of acetates ions remain on the glass after washing. They are found in random quantity during the analysis. When they are present, a precise quantitative analysis of the fluoride ions is impossible, but all other ions in solution can be analyzed. The resolutions calculated for the Bromide, Chloride and Sulphate ions are high enough to allow a quantitative analysis of these ions.

Influence of a high content of Cl⁻ on the measurement of the amount of Br⁻

Under the used conditions, the Chloride ions are eluted before the Bromide ions; consequently, for combustion matrices containing a high amount of Chloride ions, it may be difficult to measure the amount of Bromide ions, because the Chloride peak may distort the Bromide peak.

A solution coming from the combustion of a PVC material was used as a combustion matrix. It contains approximately 1000 mg/l Chloride ions (About the maximum concentration which can be met in the NF X 70-100 tests). A weak concentration of Bromide ions was added: 2.5 mg/l.



Calibration

[C] = a*Area+b		Area	Amount of Br ⁻
a=	1.56E-05	Solution 1 141241	2.57
b=	0.3705	Solution 2 144012	2.61
		Solution 3 144776	2.62
		Mean	2.60

These results show that even the highest concentration of Chloride ions do not prevent weak concentrations of Bromide ions from being correctly measured.

Specificity of the method

The goal of this step is to check that the I.L.C. method has a sufficient specificity for the Chloride and the Bromide ions. The study of specificity was carried out with solutions resulting from material combustion. These solutions thus have matrices representative of the usually analyzed solutions.

For the ions Chloride and Bromide, 5 solutions with concentrations from 1 to 20 mg/l were used. The additions carried out on these solutions are of the same order of magnitude as the initial concentrations met in the combustion matrices. For example, for a combustion matrix with 5 mg/l of Chloride ions, an addition of 5 mg/l of Chloride ions is done.

A calibration was initially carried out on the I.L.C.. Each initial solution is analyzed first to get the analyte concentration. Then, the addition is carried out using standard solutions. In this way, the added concentration is accurately known, and is called the "real" addition (v_i). The resultant solution is also analyzed. Since the initial concentration is known, the found addition is measured (r_i). For the Chloride and Bromide ions, 5 sets of data are obtained.

For both ions, the best straight line $r_i = f(v_i)$ is plotted. Its equation is of the form $r_i = b_1 * v_i + b_0$. Statistical tools allow then to check if $b_1 \approx 1$ and $b_0 \approx 0$. If these two conditions are simultaneously met, then the selectivity is correct. Calculations are detailed below.

$$\text{Residual Standard deviation } s(e) = \sqrt{\frac{\sum_{i=1}^p (r_i - \hat{r}_i)^2}{p - 2}}$$

$$\text{Standard deviation on } b_1 \text{ } s(b_1) = \sqrt{\frac{s^2(e)}{\sum (v_i - \bar{v})^2}}$$

$$\text{Standard deviation on } b_0 \text{ } s(b_0) = \sqrt{s^2(e) \left(\frac{1}{p} + \frac{\bar{v}^2}{\sum (v_i - \bar{v})^2} \right)}$$

$$t_{obs} = \frac{|b_1 - 1|}{s(b_1)} \quad \text{Check if } b_1 \approx 1: \text{ Comparison at Student's } t \text{ for 3 degrees of freedom with a 95 \% confidence (unilateral test).}$$

$$T_{obs} < t_{student}$$

$$t'_{obs} = \frac{|b_0|}{s(b_0)} \quad \text{Check if } b_0 \approx 0: \text{ Comparison at Student's } t \text{ for 3 degrees of freedom with a 95 \% confidence.}$$

$$T'_{obs} < t_{student}$$

Results

Ion	Chloride	Bromide
s(e)	4.54E-01	2.03E-01
b ₁	1.039	1.1112
s(b ₁)	3.37E-02	3.32E-02
b ₀	0.34	-0.1516
s(b ₀)	0.32	0.16
t _{obs}	1.18	3.35
t' _{obs}	1.06	0.94
t _{student (95%)}	3.18	3.18
t _{student (99%)}	5.84	5.84

For both ions, b_0 can be considered as equal to 0 with a 5 % risk. For Chloride, b_1 can be considered as equal to 1 with a 5 % risk. This risk is 1 % for Bromide.

Consequently, the method is specific for the measurement of the amount of Chloride and Bromide ions in combustion matrices.

Influence of the measurement technique on results

Principle

At the present time, the materials to be tested are degraded in a tubular furnace, and the gas effluents pass through impingers containing de-ionized water, in conformity with the NF X 70-100 standard. The analysis of the trapping solution is then carried out using titrimetry. The aim is to

prove that the two techniques (titrimetry and I.L.C.) give similar results on all the range of amount for HCl and HBr. The concentrations that have been historically met during routine tests for those two gases are:

- From 0 to 593 mg/g (for a pure PVC) for HCl and
- From 0 to 150 mg/g (very seldom higher than 50 mg/g) for HBr.

To compare the two assay techniques, some materials are first degraded with the tubular furnace according to the standard method, and the effluents are trapped in de-ionized water. Then, the analysis is carried out both by titrimetry and I.L.C..

To conclude on the influence of the analysis technique, the obtained results are analyzed by comparison of the standard deviations, then by comparison of the mean values.

Statistic tools used

As for the study of the influence of the trapping solution on the measurement of the amount of CO and CO₂, two sets of values are obtained. To state whether these sets are equal or different, statistical tests are carried out, which requires the mean value, the standard deviation and the variance, to be calculated. These calculations are done as follow:

For n measurements carried out (3 or 5 in our case):

$$\text{Mean Value } \bar{x} = \frac{\sum x_i}{n} \quad \text{Standard deviation } s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}}$$

$$\text{Variance } s^2 = \frac{\sum (x_i - \bar{x})^2}{n - 1}$$

Two tests must then be carried out to conclude: a comparison of the variances then a comparison of the mean values.

1 - Comparison of variances

The variances are statistically compared with a F-test. In this test, the ratio of the two variances ($F_{observed}$) is compared to a theoretical F-ratio ($F_{theoric}$). Under the hypothesis that the variances are equal, the $F_{observed}$ value is a Fisher variable. In this case, $F_{theoric}$ values are tabulated for different levels of probability.

$$F_{observed} = \frac{s_1^2}{s_2^2} \quad s_1: \text{ standard deviation of series 1 and } s_2: \text{ standard deviation of series 2. } s_1 > s_2 \text{ so that } f_{observed} > 1$$

It is then necessary to refer to the Fisher-Snedecor table to get the value of $F_{theoric}$:

- If $F_{observed} < F_{theoric}$ then the variances are regarded as equal,
- If not they are significantly different.

2- Comparison of mean values

n_1 and n_2 are the number of repetitions of series 1 and 2.

$$\text{Pooled standard deviation } s_p = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}$$

$$\text{Value of } t_{observed} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_p} \sqrt{\frac{n_1 \times n_2}{n_1 + n_2}}$$

This value is compared with the value of the Student's table at a degree of freedom $n = n_1 + n_2 - 2$. If $t_{observed} < t_{student}$ the mean values are regarded as equal. If not, they are significantly different.

Results

For each material, the two series of results are equivalent if the variances and the means are found as statistically equal. Then, one may conclude the assay technique has no influence to the measure for this material.

Material	[HCl] (mg/g) with titrimetry		[HCl] (mg/g) with I.L.C.		Deviation between mean values (mg/g)
	Mean Value	Std. Dev.	Mean value	Std. Dev.	
A1	4.20	1.18	4.18	0.93	0.02
B1	8.34	1.01	8.10	1.09	0.24
C1	14.40	1.69	13.93	1.44	0.47
D1	133.68	7.83	132.77	9.14	0.91
E1	-	-	-	-	-
F1	162.21	5.67	151.54	11.72	10.67
G1	248.77	1.10	232.17	3.53	16.60
H1	574.68	8.90	523.08	9.12	51.60

Material	[HBr] (mg/g) with titrimetry		[HBr] (mg/g) with ILC		Deviation between mean values (mg/g)
	Mean Value	Std. Dev.	Mean Value	Std. Dev.	
A1	33.52	2.93	33.18	2.56	0.35
E1	59.52	3.21	56.33	3.07	3.19
F1	9.52	1.82	7.84	1.46	1.69

For all materials releasing HBr and those releasing HCl between 4,12 and 156,88 mg/g, calculations show that there is no influence of the technique on the results. For two materials releasing a higher amount than 156,88 mg/g for HCl, amounts measured by ILC are approximately 10 % lower than those measured by titrimetry. For one material, the two sets of results have unequal variances and mean values. For the pure PVC (H1) tested in the last, the variances are comparable but the mean values are unequal.

Tests of comparison between ILC and titrimetry were thus carried out to be able to conclude on the equivalence of the two techniques.

Comparison between titrimetry and ILC

Solutions with 10, 15 and 20 mg/l in Chloride ions were analysed by ILC and titrimetry. They were prepared starting from a reference solution different from the solution used for the calibration of the chromatograph.

Comparison in term of repeatability

[Cl ⁻] (mg/l)	CV (%)	
	Titrimetry	ILC
9.99	1.50%	0.25%
15.08	0.19%	0.50%
19.19	1.59%	0.11%

The results are less dispersed with the Ion Liquid Chromatography. The repeatability is better with Ion Liquid Chromatographie than with titrimetry.

Comparison in term of freedom from bias

[Cl ⁻] (mg/l)	Titrimetry		ILC	
	Results (mg/l)	Bias (%)	Results (mg/l)	Bias (%)
9.99	9.97	0.18%	9.49	5.01%
15.08	15.32	1.58%	14.61	3.15%
19.19	19.66	2.44%	18.28	4.76%

The results obtained by titrimetry are higher than those obtained by ILC. The bias obtained by ILC is important, so the calibration can be questioned. The solution used for the calibration was thus checked. It proved that the bias on this standard solution was important. Therefore, the conclusion is that the traceability of the commercial standards is of primary importance for the analysis and the commercial standard solutions do not systematically give satisfaction.

ILC and the titrimetry can be used indifferently to measure the amount of the Chloride and Bromide ions in the studied ranges of concentrations. For contents of HCl from 0 to 549 mg/g and of HBr from 0 to 60 mg/g, the ILC can be used for the analysis of the gas effluents. The content of the standard solutions is prone to many future works.

Influence of the trapping solution on the trapping of HCl and HBr

The aforementioned conclusion is that combustion matrices solutions can be analysed using I.L.C. The aim is now to prove that the alternate use of Hydrogen Peroxide supplemented water has no influence on the trapping of HCl and HBr, compared to Water. The diagram below summarizes how the influence of the trapping solution has been studied for each material.

For each material, five combustions are carried out with water as trapping solution. Five new combustions are then carried out using hydrogen peroxide supplemented water as trapping solution. The analysis is then carried out by ILC on the ten solutions. The results are then compared using statistical tests.

The materials have been selected in order to cover concentrations for HCl and HBr from the lowest to the highest concentrations. These materials

have also been used in the preceding part to study the influence of the assay technique.

Materials	[HCl] (mg/g) in water		[HCl] (mg/g) in hydrogen peroxide supplemented water		Deviation between mean values (mg/g)
	Mean Value	Std. deviation	Mean Value	Std. deviation	
A2	4.18	0.93	4.28	2.20	0.10
B2	-	-	-	-	-
C2	151.54	11.72	164.84	8.88	13.30
D2	232.17	3.53	238.42	2.82	6.26
E2	523.08	9.12	528.45	9.53	5.37

Materials	[HBr] (mg/g) in water		[HBr] (mg/g) in hydrogen peroxide supplemented water		Deviation between Mean Values (mg/g)
	Mean Value	Std. deviation	Mean Value	Std. deviation	
A2	33.18	2.56	37.12	1.61	3.94
B2	55.22	2.10	55.18	1.13	0.04
C2	7.84	1.46	7.89	1.07	0.06

For all these materials, calculations show that there is no influence of the trapping solution, whatever the amount of HCl and HBr is.

Consequently, the conclusion is that both the technique of analysis and the trapping solution do not have any influence on the analyses of HCl, HBr, CO and CO₂, whatever their amount.

- The analyses CO, CO₂ can then be carried out continuously during the combustions carried out with hydrogen peroxide supplemented water to trap HCl, HBr and SO₂.
- The amount of the trapped species Cl⁻, Br⁻ and SO₄²⁻ in the combustion matrix may then be measured by I.L.C..

Linearity study for Cl⁻, Br⁻ and SO₄²⁻

To study the linearity, a calibration curve with 5 levels of concentration is carried out for each analyte. Each solution is prepared 5 times. For each ion, 25 solutions are thus analyzed. The study of the linearity consists in checking that a model of regression explains the data. The study starts with a linear model. If this model does not explain the data, then a polynomial model of degree 2 is used. If only a polynomial model explains the data, it should be understood why the response given by the apparatus is not linear. The statistical calculations carried out to check the linearity are detailed below.

Statistical analyse

$$\text{Mean Value } \bar{y}_i = \frac{\sum_{i=1}^p y_i}{p} \quad \text{Standard deviation } S_{y_i} = \sqrt{\frac{\sum_{i=1}^{i-1} (y_i - \bar{y}_i)^2}{p-1}}$$

$$b_1 \text{ and } b_0 \text{ (for linear model)} \quad b_0 = \frac{\sum (x_i - \bar{x}_i)(y_i - \bar{y}_i)}{\sum (x_i - \bar{x}_i)^2} \quad b_1 = \bar{y}_i - b_1 \times \bar{x}_i$$

$$\text{Response of the model } \hat{y}_i \quad \hat{y}_i = b_1 \times x_i + b_0$$

$$\text{Non-linearity residuals } \bar{y}_i - \hat{y}_i \quad \text{Repeatability residues } y_i - \bar{y}_i$$

$$\text{Sum of the squares of the deviations For } y_i, \quad SCE_{y_i} = \sum (y_i - \bar{y}_i)^2$$

$$\text{Degrees of freedom} \quad df_{\text{Explained}} = df_{\text{Model}} - 1 \quad df_{\text{residual}} = np - p$$

$$df_{\text{non-linearity}} = p - 2 \quad df_{\text{Total}} = np - 1$$

$$\text{Median squares} \quad MS = \frac{SCE}{df}$$

$$F_{\text{obs values}} \quad F_{\text{obs explain}} = \frac{MS_{\text{Explained}}}{MS_{\text{Residual}}} \quad F_{\text{obs Non linearity}} = \frac{MS_{\text{Non linearity}}}{MS_{\text{Non linearity}}}$$

The coefficient of regression r² is not sufficient to validate the used model; it is also necessary to carry out a variance analysis:

- Stage 1: Checking of the validity of the regression; If $F_{\text{obs explain}} > F_{95\%}$ then the regression is validated.
- Stage 2: Checking of the linearity; If $F_{\text{obs Non-linearity}} < F_{95\%}$ then the linearity is validated.

Results

Case of the ion Chloride

The straight-line relationship does not explain the data because the residuals of non-linearity are too important. By using a polynomial model of degree 2, the residues of non-linearity are slightly higher than $F_{theoric}$.

It is thus necessary to run the study of linearity again, taking into account the uncertainty due to the preparation of the standard solutions. For each standard solution, uncertainty relating to the volume of mother solution taken, the volume of flask and the concentration of the standard was given. Each result of peak area was thus modified in order to decrease the difference between the experimental values and the model. By taking account of uncertainties due to the preparation of the standard solutions, a polynomial model of degree 2 (second order) explains the data.

Case of the ion Bromide

Like the case of ion Chloride, the straight-line does not explain the data because the residuals of non-linearity are too important. A polynomial model of degree 2 explains the data.

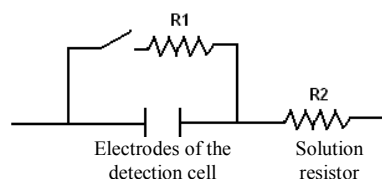
Case of the ion Sulphate

Like the case of ions Chloride and Bromide, the straight-line does not explain the data because the residuals of non-linearity are too important. A polynomial model of degree 2 explains the data.

Conclusion on linearity

To measure the amount of Cl⁻, Br⁻ and SO₄²⁻ in combustion matrices using ion liquid chromatography, a calibration with a second order polynomial model must be used.

Theoretical explanation to the non-linearity :



Equivalent circuit of a conductimetric detector

The detector measures G , conductivity of the solution: $G=1/R_2$.

The conductivity of the solution depends on the detection cell, the analytes and the matrix. Specific conductivity k depends only on the solution:

$k = G \times K_{cell}$. The constant ($K_{cell} = \text{length/surface}$) depends on the parameters of the detection cell, and is determined by the manufacturer. Conductivity k is the total conductivity read on the apparatus, i.e. the conductivity of the solution before its entry in the ion suppressor.

Equivalent conductivity $\wedge = \sum (u_+ + u_-)$ is characteristic of the studied analyte.

\sum is the constant of Faraday and u_+ and u_- are the mobility of the ion in the solution:

$$\begin{aligned} \wedge_{Cl^-} &= 76 \text{ S.cm}^2/\text{eq} \\ \wedge_{Br^-} &= 78 \text{ S.cm}^2/\text{eq} \\ \wedge_{SO_4^{2-}} &= 80 \text{ S.cm}^2/\text{eq} \end{aligned}$$

The detector thus has a very close sensitivity for the studied ions. Specific conductivity is proportional to the conductivity of the present species and to their concentration: $k = \sum_i (\wedge_i * C_i)$. Equivalent conductivity is characteristic of an ion with infinite dilution because the surrounding of ions by other ions of opposite charge is neglected.

If the concentration increases, the mobility of the ions then decreases because this phenomenon is accentuated. The equivalent conductivity of the ion decreases as well as specific conductivity. This is why a variation with the linearity is observed when the concentration in analyte increases. It is therefore important to work on a narrow interval of concentration. Nevertheless, the second order polynomial model allows to work on the range of concentrations used in routine at LNE.

Determination of limits of detection

The limit of detection was determined starting from the background noise generated by the chromatographic system. To observe the background noise, chromatograms issued from demineralised water injection were used. Water is not much retained by the column and is eluted after around 2'30 minutes in the studied chromatographic conditions (a fall of conductivity is observed). From the 3rd to the 11th minute, the variations of conductivity are only due to the background noise. The background noise is measured on this interval.

There are 3 methods to calculate the limit of detection:

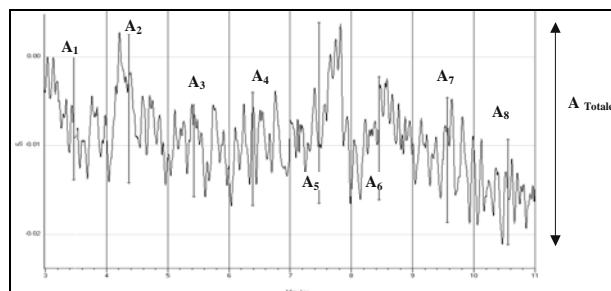
1. Measure the amplitude of the background noise on the whole interval: Background noise (BN) corresponds to the maximal observed amplitude.
2. Measure the amplitude of the background noise every minute on the elapsed 1 min interval. The mean value of these amplitudes is calculated and considered as representing background noise:

$$BN = \frac{\sum_{i=1}^n A_i}{n}$$

3. Measure the amplitude of the background noise every minute on the elapsed 1 min interval. The standard deviation of these amplitudes is then considered to be the background noise:

$$BN = \sqrt{\frac{\sum_{i=1}^n (A_i - \bar{A})^2}{n-1}}$$

Then LD is equal to 3 times the background noise. The third method allows to evaluate the background noise with the best precision, because it considers the variations of background in function of retention time. The limits of detection of the ions Chloride and Bromide were thus calculated using this method:



The limit of detection obtained is expressed in μS , the measurement unit of the detector. To connect this value to a unit of concentration, a solution with 0.1 mg/l in ions Chloride and Bromide was injected. 3 chromatograms produced in one month of interval were used to be best freed from the time influence factor or from the ageing or the contamination of the column. The evaluation of the background noise starting from the analysis of a water solution of quality 1 gave an average background noise of $2.83 \cdot 10^{-3} \mu\text{S}$.

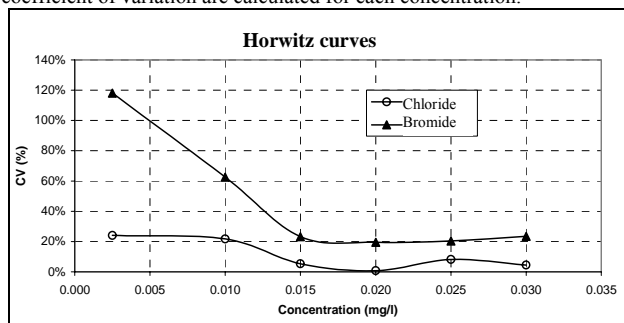
The limit of detection is regarded as 3 times the standard deviation of these measurements. For a variation of conductivity higher than this value, the probability that this variation is due to the presence of a compound is higher than 99.9 %. In this case, the limit of detection is equal to $8.50 \cdot 10^{-3} \mu\text{S}$. After calculation, limit of detection corresponding to this value is given in table below:

	Peak height with 0.1 mg/l solution	LD (mg/l)	LD (ng)
Chloride	0.181 μS	0.005	0.24
Bromide	0.050 μS	0.017	0.84

These limits of detection are only valid for the conditions of analysis that have been used : flow rate, composition of mobile phase, column and detector. In the NF X 70-100 (April 2006) standard, the LD of the Chloride and Bromide ions are set at 0.1 mg/l. The results obtained here are definitely lower. The following stage consists in validating these results.

Confirmation of limits of detection

To confirm a limit of detection, solutions with Cl⁻ and Br⁻ with concentration close to the theoretical LD are analyzed. Each solution is analyzed several times. The mean value, the standard deviation then the coefficient of variation are calculated for each concentration.



For the Chloride and Bromide ions, the $CV=f([Cl^-])$ and $CV=f([Br^-])$ curves, called curves of Horwitz, are drawn. The limit of detection is the concentration corresponding to $CV=50\%$. These Horwitz curves generally allow a simple graphical determination of LD for each ion.

For chloride, the CV is weak and always less than 50%. At concentration levels $C=0.0025$ and $C=0.0100$ mg/l, the surfaces of the peaks are comparable. Horwitz method seems to be not adapted to an ion like Chloride in these analytical conditions. The LD of the Chloride ions is nevertheless close to these values. The previous study allowed to determine theoretical $LD_{Cl^-} = 0.0050$ mg/l. This value is close to the values obtained in experiments (between 0.0025 and 0.010 mg/l.). To get more confidence on the value, the limit of detection of the Chloride ions is set at 0.01 mg/l.

For bromide, the CV decreases from about 120% to 20%. The method is more appropriate for this ion in these analytical conditions. It allows to estimate a LD_{Br^-} of 0,012 mg/l for $CV=50\%$. Nevertheless, for concentrations in Bromide ions from 0,0025 to 0,0150 mg/l, the peak surfaces are too low to be correctly dissociated from the background noise. For a concentration of 0.020 mg/l, detection is carried out with a CV close to 20 %. The LD of the Bromide ions thus lies between 0.015 and 0.020 mg/l. This interval includes the theoretical value previously found ($LD_{Br^-} = 0.017$ mg/l). For more confidence, the limit of detection for the Bromide ions is set at 0.02 mg/l.

The analysis of the Chloride and Bromide ions is carried out with a calibration ranging between 1 and 20 mg/l. Only the solutions whose Bromide and Chloride concentrations are included in this range of calibration can be given with precision. The measurement of the amount of the Chloride ions for concentrations ranging between 0.01 and 1 mg/l and of the Bromide ions for concentrations ranging between 0.02 and 1 mg/l can be carried out, provided that an adequate calibration is carried out.

Determination of uncertainties

The uncertainties given in the table below are uncertainties due to the measurement. Influences of the material were neglected. The objective is to compare I.L.C. uncertainties with titrimetry values presented in the literature and previous studies. This uncertainty is presented below in the propagation table [7].

Factor Xi	value Xi	Uncert. u(Xi)	u(Xi)/Xi
Mass of the sample m_{sample} (g)	about 1g	$2.31 \cdot 10^{-4}$	$2.31 \cdot 10^{-4}$
Volume of 500 ml flask V_{flask} (ml)	500	$2.64 \cdot 10^{-1}$	$5.28 \cdot 10^{-4}$
Uncertainty on the dilution d	-	-	$6.78 \cdot 10^{-3}$
M_{gas} (g/mol)	M(HCl)	36.46094	$5.79 \cdot 10^{-4}$
	M(HBr)	80.91194	$5.79 \cdot 10^{-4}$
$M_{analyte}$ (g/mol)	M(Cl ⁻)	35.453	$1.00 \cdot 10^{-3}$
	M(Br ⁻)	79.904	$1.00 \cdot 10^{-3}$
C_{flask} (mg/l)	[Cl ⁻]	Variable	$6.13 \cdot 10^{-2}$
	[Br ⁻]	Variable	$6.13 \cdot 10^{-2}$

C_{flask} is calculated as follow:

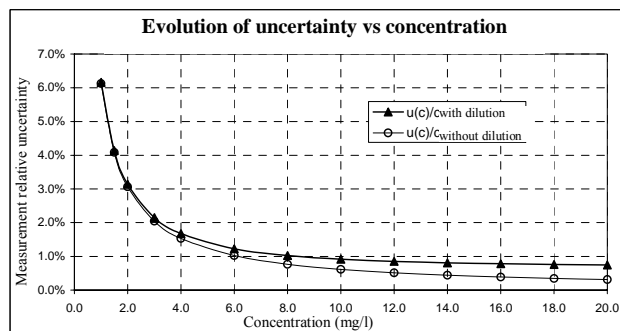
$$Area = b_2 \times (C_{flask})^2 + b_1 \times C_{flask} + b_0$$

Final concentration:

$$C = \frac{C_{flask} \times V_{flask} \times M_{gas} \times d}{m_{sample} \times M_{analyte} \times 1000}$$

Uncertainty is calculated as the sum of variances: $\frac{u(C)}{C} = \sqrt{\sum_i \left(\frac{u(x_i)}{x_i}\right)^2}$

Uncertainty due to measurement is a function of the concentration in analyte. It is traced below (the curves are almost identical for Chloride and Bromide)



In the literature, the uncertainty of measurement using titrimetry is estimated at 4%. For concentrations in analyte higher than 1.5 mg/l, uncertainty due to measurement in ILC is lower than this one.

Conclusions and evolutions

The new method has brought several improvements in the laboratory work, both in quantity and in quality. The key points are listed below.

Reduction in the number of analysis: The analysis of CO/CO₂/HCl/HBr and the analysis of SO₂ have been grouped together, increasing productivity. For a same amount of work as before, more gas are analysed, leading to a significant decrease of the lead-time for the tests.

Increase in the reliability of the results: The measurement of the amount of Cl⁻ and Br⁻ ions, when simultaneously present in the combustion matrices, using Ion Liquid Chromatography, allowed to be freed from the bias inherent to the titrimetry.

The NF X 70-100 (April 2006) standard gives limits of detection for the Chloride and Bromide ions: $LD_{Cl^-}=4$ mg/l and $LD_{Br^-}=8$ mg/l, without further information. The studies presented here allowed to determine the limits of detection using I.L.C.: $LD_{Cl^-}=0.01$ mg/l and $LD_{Br^-}=0.02$ mg/l. The limits of detection of the ions Chloride and Bromide have been largely improved.

Uncertainty due to the method of measurement is lower than 4 % for concentrations in analyte higher than 1.5 mg/l, which is itself under the conventional limit of detection given in the standard. This value was 4 % with the use of the titrimetry. The measuring accuracy thus was improved overall.

This method has been validated to be used in routine work. Its installation allowed to decrease the workload of the operators and to reduce the time of the analysis. The margin released on these commercial tests thus could be appreciably increased. Moreover, by replacing the titrimetry, the Ion Liquid Chromatography improved the quality of the measurements.

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