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# Determination of Hydrogen Chloride Concentration during Decomposition and Combustion of Textile Fabrics Used as Interior Decorations

## Abstract

In this paper, we present the difficulties in determining chloride ions in the presence of significant amounts of cyanide ions in 0.1 M of NaOH solution by classic methods. A new method of the Cl<sup>-</sup> determination in a strong alkaline environment has been devised. The results obtained confirmed the effectiveness of this technique.

**Key words:** emission of toxic products of decomposition and combustion, hydrogen chloride, hydrogen cyanide, capillary electrophoresis.

finishing materials or other textiles used in flats, public buildings or public transport, it is very important to have knowledge and proper analysis of toxic gases produced during fire. As only scarce experimental data are available on the toxic gas hazards resulting from the combustion of textiles under fire conditions, the decomposition and combustion of various final textiles were examined using fabrics made of typical raw materials such as polyacrylonitrile, polyamide, polyester, polypropylene, rayon, cotton and wool. The materials to be tested were selected as representatives of common textiles in everyday use, such as elements used in interior design (including accommodation).

Due to the specific characteristics of textile fabrics (the possible simultaneous high HCN and HCl concentrations in combustion products), the results obtained by the methods recommended by the standard aroused doubts, and it was therefore necessary to search for other possibilities to determine these compounds.

to a sample previously acidified with nitric acid, followed by the addition of ferric ammonium salt. The reaction is selective and specific for hydrogen chloride if the tested sample contains only chloride ions and no other ions such as bromide, iodide, fluoride and cyanide, as all of them react with mercury ions [3,4]. However in practice, the samples tested are a mixture of various ions and contain at least cyanide and hydroxide ions; thus, both chlorides and cyanides will react with mercury ions. Chlorides and a mercury salt solution precipitate white mercuric chloride (Figure 2)

$\text{Hg}^{2+} + 2\text{Cl}^- \rightarrow \text{Hg}(\text{Cl})_2\downarrow$ ,  
while cyanides form a soluble mercury complex (Figure 1)

$\text{Hg}^{2+} + 2\text{CN}^- \rightarrow \text{Hg}(\text{CN})_2\downarrow$ .  
Complex  $[\text{Hg}(\text{CN})_2]$  is only precipitated from relatively concentrated solutions.

The sparingly soluble salt starts to precipitate when the ion concentrations in solution whose product is equal to the solubility product of that salt are exceeded. If two or more ions are present in solution, reacting with the ion added to this solution with the formation of a sparingly soluble precipitate, then the compound whose solubility product is lowest will be first to precipitate, followed by subsequent pre-

## Introduction

Fire is undoubtedly a great danger both to people directly within its area and to the wider natural environment. In the case of fire in apartment buildings, public places or means of transport, there are several serious hazards. In addition to burns, the major cause of most fatal accidents during fires is the emission of the toxic products of decomposition and combustion. These principally include hydrogen chloride and hydrogen cyanide [1].

During the approval procedure for use of building materials, textile interior

## Determination of HCl in Combustion Products

The method of chloride determination recommended by standard [2] consists in mercuric thiocyanate being added

Table 1. Reaction of formation of the  $\text{Hg}(\text{Cl})_2\downarrow$  and  $\text{Hg}(\text{CN})_2\downarrow$  described as pH changes.

Amount of ml $\text{Hg}^{2+}$ solution added	Concentrations and exponents				$\text{pHg}^{2+}$
	$[\text{CN}^-]$	$\text{pCN}^-$	$[\text{Cl}^-]$	$\text{pCl}^-$	
0	0	0	0	0	40.00
	0.000096	4.02	0	0	35.98
2	0.000000012	8.91	0	0	31.09
	$1 \times 10^{-28}$	29.5	0.000000038	8.5	10.50

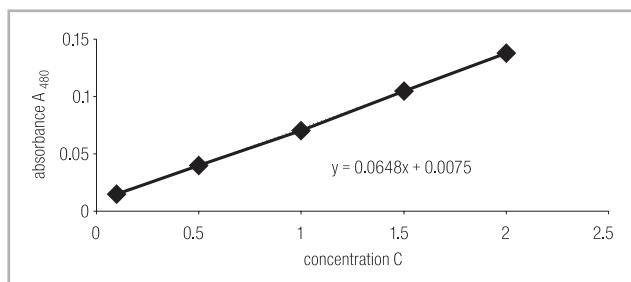


Figure 1. Determination of cyanides by the thiocyanate-chloride method.

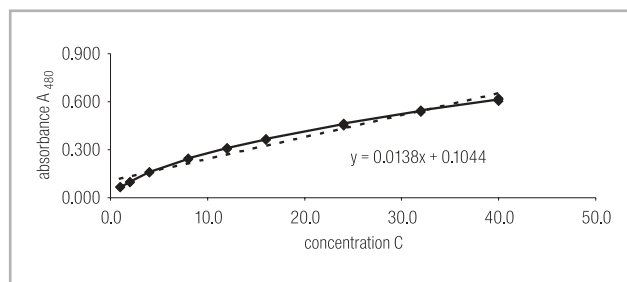
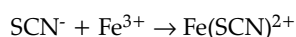
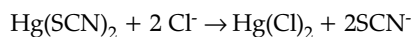


Figure 2. Determination of chlorides by the thiocyanate-chloride method.

precipitates in the sequence of increasing values of  $K_{SO}$  [3,4]. An excess of the precipitant ions supports the more complete precipitation of the ions which are being precipitated. The course of the reactions taking place during the determination of chlorides by this method depends on the presence of various ions including cyanides.



It is possible to calculate the precipitated ion concentration if the solubility product of the compound being formed is known. The course of the processes taking place during the determination of chlorides is considered using an example of reaction including 2 ml of  $\text{Hg}(\text{SCN})_2$  with a concentration of 1  $\mu\text{g}/\text{ml}$   $\text{Cl}^-$  [molar concentration of 0.00032M  $\text{Hg}^{2+}$ ] and 10 ml of NaCl standard solution with a concentration of 10  $\mu\text{g}/\text{ml}$   $\text{Cl}^-$  [molar concentration of 0.0003M  $\text{Cl}^-$ ] in the presence of 1 ml of  $\text{CN}^-$  ions with a concentration of 2.5  $\mu\text{g}/\text{ml}$  [molar concentration of 0.000098M  $\text{CN}^-$ ] (Table 1, Figure 3).

The reaction error in the presence of two reaction components at the same time results from the fact that the more easily soluble precipitate begins to precipitate before the precipitation of the more sparingly soluble component is finished.

From the consideration stated above, it follows that when using the method recommended by the mentioned standard, all the obtained results of chloride concentration were considerably over-assessed depending on the cyanide content in the combustion products, as is the case with the combustion of rubber (element of interior finishing). This combustion may result in the emission of gas mixtures containing chlorine, hydrogen chloride, hydrogen cyanide, cyanides, thioalco-

hols, aldehydes and sulphur dioxide [1]. Thus, the use of the method discussed above may give false results. For instance, during the combustion of polyurethanes, polyamide, wool, silk and polyacrylonitrile, substances including hydrogen cyanide,  $\text{NO}_x$ , CO,  $\text{CO}_2$ ,  $\text{NH}_3$ , amines, acrylonitrile, cyanates are emitted [1], and the toxic products evolved have no hydrogen chloride. The use of the thiocyanate method in this case shows the presence of chlorides, and only hydrogen cyanide was emitted, not hydrogen chloride.

Another method for the determination of chloride ions is the precipitation reaction [5-7] in solutions of dilute nitric acid by means of a standardised  $\text{AgNO}_3$  solution standard [7]. The reaction is specific for chlorides, but also ions such as bromides, iodides, fluorides and cyanides can react in the same way. It seldom happens in environmental assessments that these ions appear together in significant concentrations, but in the case of the determination of combustion products of textiles, this is a very common phenomenon.

Attempts to determine chloride ions by means of an ion-selective electrode also fail to provide satisfactory results. This procedure of determination is recommended by standard [8]. Combustion products pass through scrubbers containing water instead of 0.1 M NaOH, while this standard clearly recommends that even insignificant quantities of cyanides should be removed by oxidation with hydrogen peroxide or by complex formation with nickel.

It is generally assumed that the ions which form insoluble salts with ions present in the sensor element of the electrode, and/or ions which form strong complex compounds with the components of the electrode sensor elements, disturb the electrode's response. For example, in measurements with a chloride-sensitive electrode, the content of bromides, iodides, cyanides

and sulphides must be checked since corresponding silver salts are less soluble than the chloride which forms the electrode sensor element. The maximum concentration of disturbing ions which may be present in a sample without causing disturbance to the ion-selective electrode response can be easily calculated from the value of solubility products or the complexity constant of corresponding compounds.

It is seen in the examples discussed above that it is impossible to properly determine chlorides in the presence of considerable quantities of cyanides by all the conventional methods. We thus expected that the proper determination of chlorides could only be performed by a completely different method, which should be based on a procedure which eliminates the necessity for specificity and selectivity reactions of a compound, e.g.,  $\text{AgNO}_3$  or  $\text{Hg}(\text{SCN})_2$  in relation to chloride ions.

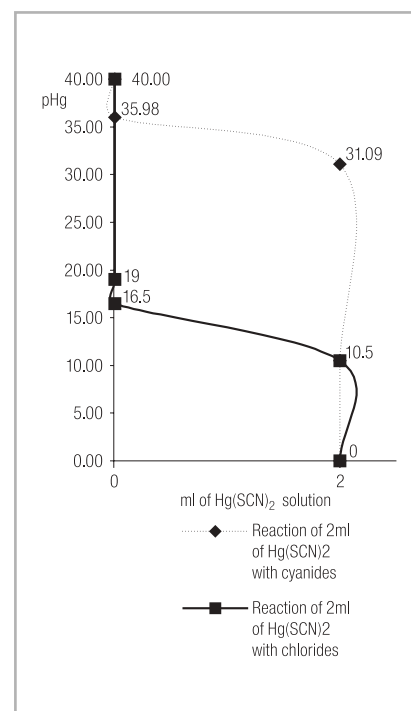
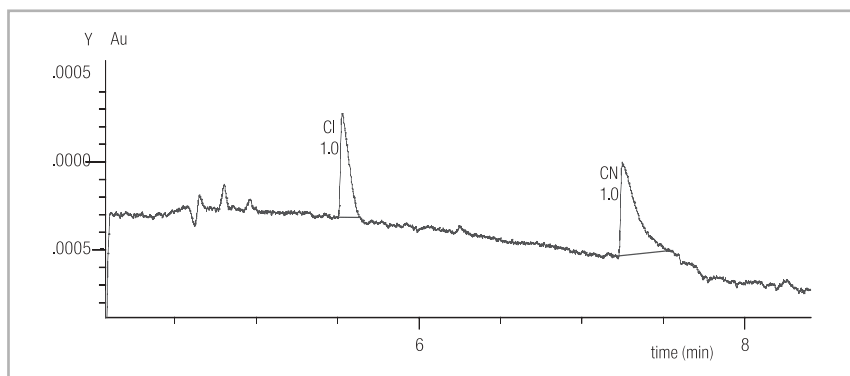
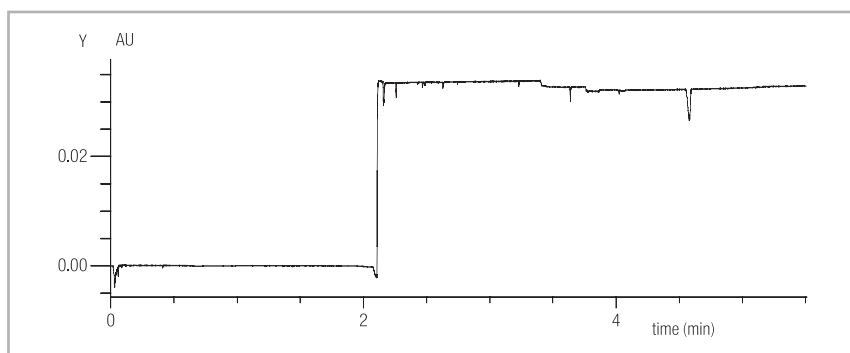


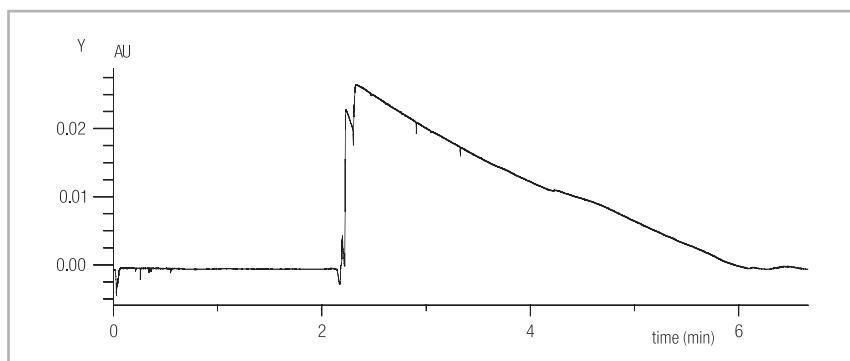
Figure 3. Scheme of reactions taking place in the mixture of chlorides and cyanides with mercury ions.



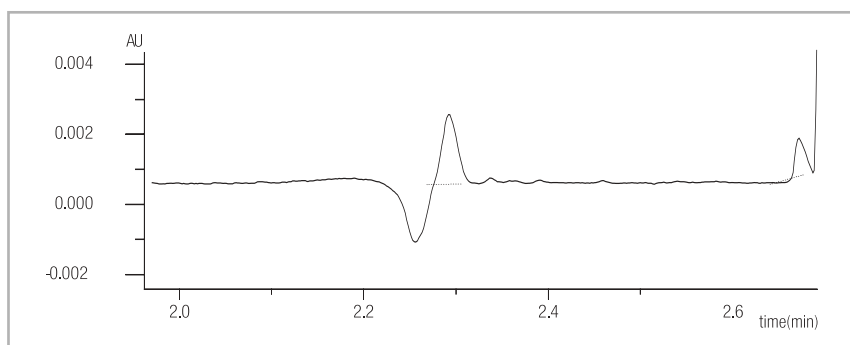
**Figure 4.** Electropherograms of cyanide and chloride mixture in an aqueous matrix. Measurement parameters: 1 mg/l Cl<sup>-</sup>, 1 mg/l CN<sup>-</sup>, 3 sec hydrodynamic injection, voltage -15 kV, 14 μA, temperature 25°C, pH 8.



**Figure 5.** Electropherograms of cyanide and chloride mixture in 0.1 M NaOH. Measurement parameters: 10 mg/l of Cl<sup>-</sup>, 5 mg/l of CN<sup>-</sup> in 0.1 M/l NaOH, 4 sec hydrodynamic injection, voltage -30 kV, 15 μA, temperature 30°C, pH 8.



**Figure 6.** Electropherograms of cyanide and chloride mixture in 0.01 M NaOH. Measurement parameters: 10 mg/l of Cl<sup>-</sup>, 5 mg/l of CN<sup>-</sup> in 0.1 M/l NaOH 1:10, 4 sec hydrodynamic injection, voltage -30 kV, 15 μA, temperature 30°C, pH 8.



**Figure 7.** Electropherograms of cyanide and chloride mixture in 0.005 M NaOH. Measurement parameters: 10 mg/l of Cl<sup>-</sup>, 5 mg/l of CN<sup>-</sup> in 0.1 M/l NaOH 1:20, 4 sec hydrodynamic injection, voltage -30 kV, 15 μA, temperature 30°C, pH 8.

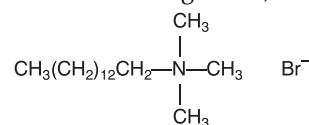
Such a property is shown by capillary electrophoresis (CE).

## Determination of Chlorides and Cyanides with the Use of Capillary Electrophoresis

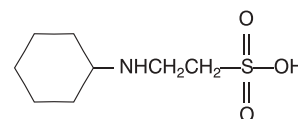
The highly efficient technique of capillary electrophoresis is a new analytical tool. It differs from the remaining techniques as it utilises the behaviour of molecules in the electrical field, which causes mixture components to separate [9]. The analysis is carried out in a thin quartz capillary whose internal diameter corresponds to that of a human hair.

In the measurements carried out by the authors which made it possible to determine the chlorides and cyanides, a buffer with the following composition was used:

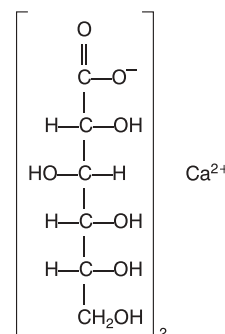
- sodium chromate Na<sub>2</sub>CrO<sub>4</sub>·4H<sub>2</sub>O with a concentration of 4 mM;
- tetradecylmethylammonium bromide (TTAB) with a concentration of 0.25 mM, which was transformed into a hydrolysed form (TTAOH) with an ion-exchange resin;



- CHES, 2-[N-cyclohexylamine]-ethan sulphonate with a concentration of 10 mM;



- calcium salt of glyconic acid with a concentration of 0.1 mM.



In order to identify peaks in the electropherogram, the spectra of chlorides and cyanides were at first taken into an aqueous matrix, using standard ion solutions of Merck® and a capillary with a diameter of 75 μm.

The electropherogram shown above (Figure 4) indicates that it is possible to determine chloride and cyanide ions by use of the electrolyte mentioned. Then, the effect of the matrix alkalinity

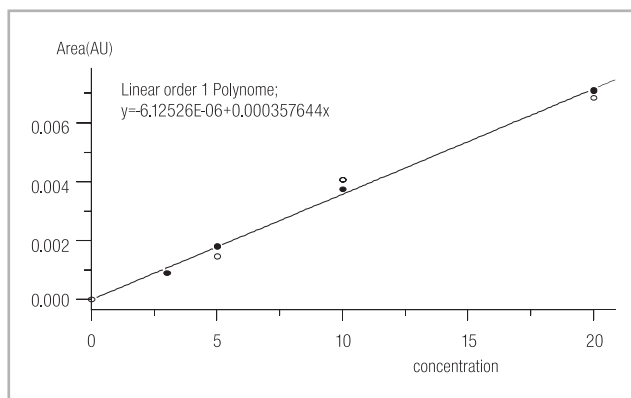


Figure 8. Curve for chloride ions.

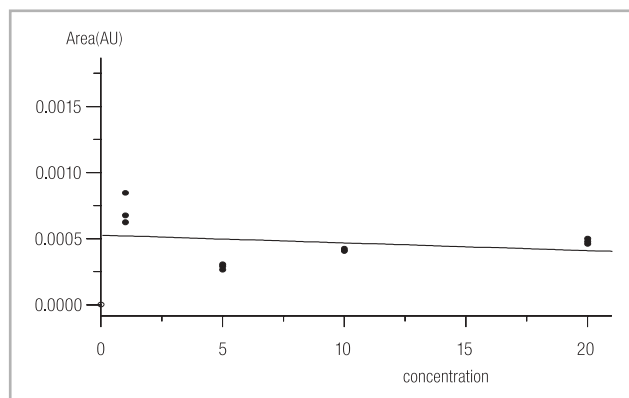


Figure 9. Curve for cyanide ions.

on the curve shape was analysed. To that end, a solution was prepared containing 1 mg/l of  $\text{Cl}^-$ , 1 mg/l of  $\text{CN}^-$  in 0.1 M NaOH in order to take spectra from it and its dilutions (1:10 and 1:20 diluted with water) (Figures 5-7). When the solution was diluted with water to a ratio of 1:20, two peaks appeared, so further dilution was considered unnecessary.

In order to identify the peaks, a calibration curve was prepared under the following conditions: 5 s hydrodynamic injection, -15 kV, 15 mA, 25°C, a chromate buffer of 4 mM, 0.25 mM TTAB.

The calibration solutions were prepared in 0.1 M NaOH and then they were diluted with water to a ratio of 1:20:

- 5 mg/l of  $\text{Cl}^-$ , 5 mg/l of  $\text{CN}^-$
- 10 mg/l of  $\text{Cl}^-$ , 10 mg/l of  $\text{CN}^-$
- 20 mg/l  $\text{Cl}^-$ , 20 mg/l of  $\text{CN}^-$
- 3 mg/l of  $\text{Cl}^-$ , 1 mg/l of  $\text{CN}^-$

Next, calibration curves for particular anions were prepared (Figures 8 and 9). In the case of the calibration curve for cyanide ions, there is no correlation between the concentration and the peak surface - these peaks are not derived from these ions. To verify this

thesis, electrophoregrams were made again under the same conditions for the following solutions (Figure 10):

- 1 mg/l of  $\text{Cl}^-$ , 1 mg/l of  $\text{CN}^-$  in an aqueous matrix,
- 1 mg/l of  $\text{Cl}^-$ , 1 mg of  $\text{CN}^-$  in a matrix of 0.1 M NaOH diluted with water to a ratio of 1:20.

Additional determinations were carried out after addition to the 0.1 M NaOH solution diluted to a ratio of 1:20, two solutions with concentrations of 25 mg/l and 50 mg/l of  $\text{CN}^-$ ; no significant differences were observed in the electrophoregrams (Figure 11).

Chloride ion as an ion of high mobility appears first at the detector window, while cyanide ion has a lower mobility and a longer migration time.

This means that in the solution in the presence of hydroxide ions - which are considerably more numerous than cyanide ions (to a proportion of around 1:4000) - the peaks of  $\text{CN}^-$  and  $\text{OH}^-$  ions are superimposed, and this in turn means they cannot be detected by the detector.

To verify the method described above, determinations of chloride ions were performed in samples (containing only these ions) containing toxic products of decomposition and combustion of materials according to standard [2] and by the electrophoretic method.

The results obtained are given in the form of a unit square (Figure 12) and the calculated regression coefficient was compared to unity; using standard [10], it was shown that the differences resulting from the determinations obtained by the methods compared can be considered insignificant.

## Summary

While testing the products of combustion of textile materials used for interi-

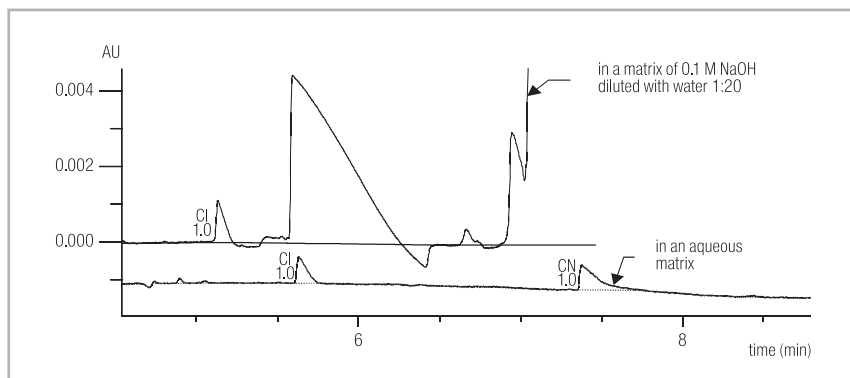


Figure 10. Electrophoregrams of cyanide and chloride mixture in an aqueous matrix and in 0.1 M NaOH after dilution in ratio of 20:1.

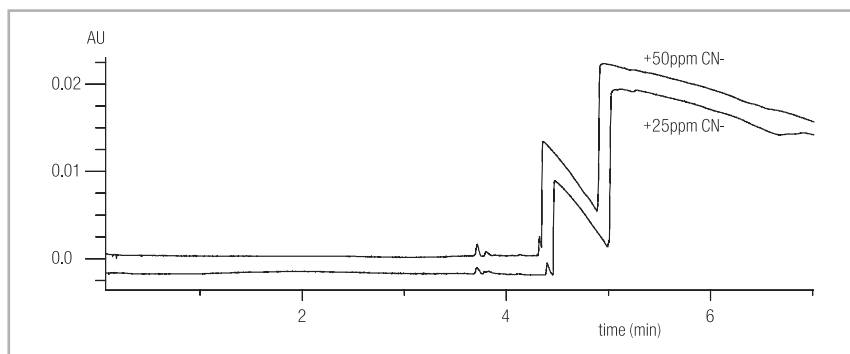


Figure 11. Electrophoregrams of cyanide and chloride mixture of concentration 25 and 50 mg/l in 0.005 M NaOH.

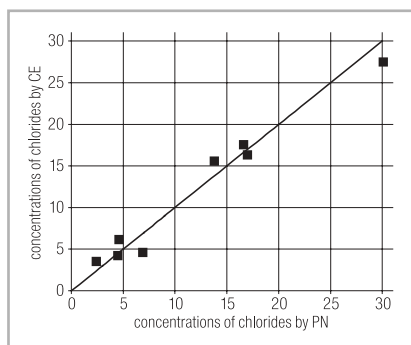


Figure 12. Diagram illustrating the differences between the two methods.

or decorations, due to the character of the compounds and their toxicity, it is necessary to determine hydrogen cyanide and chloride in the gases emitted, which can be successfully absorbed in scrubbers containing 0.1 M NaOH solution.

The methods used so far for determining hydrogen cyanide and chloride fail to provide satisfactory results. Various standards which describe the determination of decomposition and combustion products absorbable in sodium hydroxide solution use different methods of HCl and HCN determinations.

In all these procedures, except the Polish Standard [2] in the case of HCl, the condition is given that the reactions carried out in order to determine chlorides are not specific only for these ions, but also for cyanides (as is the case with the thiocyanate method [2], the precipitation method [7] and the ion-selective electrode [8]). It was therefore decided to use capillary electrophoresis for the determination of chloride ions, and satisfactory results were obtained.

However, capillary electrophoresis proved unsuitable for cyanides, due to the strongly alkaline medium (0.1 M NaOH) in which these ions must be determined.

These unsatisfactory effects prompted us to search for methods which would provide better results than those obtained by the method given in standard [2].

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