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IMPROVEMENT OF THE MICROCOULOMETRIC TITRATION METHOD ANALYTICAL CHARACTERISTICS FOR A DETERMINATION OF CHLORIDE COMPOUNDS IN PETROLEUM PRODUCTS

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Abstract
Using a microcoulometric titration system 120 Dohrmann, provided with automated modules for sampling, reliable procedures for determination of chloride compounds in liquid petroleum products – reformats, catalytically cracked gasoline, virgin naphta, diesel oils, aromatic industrial hydrocarbons and hydrocarbon gaseous (0.1-5 $mg.kg^{-1}$ Cl), and in polymeric products (above 1 $mg.kg^{-1}$Cl) were developed. The mean recovery of chloride using chlorobenzene as standard for: products with ≤ 0.5 $mg.kg^{-1}$ Cl is 99.7 %; for products with ≥1 $mg.kg^{-1}$ Cl content is 93 %; for aromatic hydrocarbons is 94 %; for polypropylene is 98%. A comparison, of the results within the micro-coulometric oxidative pyrolisis method and a spectrophotometrical method with preliminary burning of samples in Wickbold apparatus was also performed.

Key words: *chloride compounds, petroleum products, microcoulometric titration*

1. Introduction

The organic chloride compounds are well known as catalytic poisons and potentially damaging to refinery processes. Organic as well as inorganic chloride compounds even in micro-levels can prove harmful to equipment and reactions in processes involving hydrocarbons. Maximum chloride levels are specified for process streams and for petroleum products.

The determination of chloride content in complicated matrix, such as petroleum products, is a challenge for analysts, despite the availability of sophisticated instrumental techniques and standard methods at a present.

Due to its intrinsic characteristics – high accuracy and quickness, the microcoulometric titration method of determination of chlorine content in petroleum products is an attractive technique. The improved microcoulometric titration system MCTS-120 Dohrmann performs a run of analysis within a 15 minutes, while the alternative methods such as the potentiometry or colometry after burning of the samples in Wickbold apparatus [1,10] and after reduction with sodium biphenyl I[2,3] involve complex and prolonged procedures for preparation of the samples with large volumes.

In the standard methods for microcoulometric titration of chloride compounds in petroleum distillates [4] and in aromatic hydrocarbons and related chemicals [5] the specified concentration ranges and corresponding precision are related to above 1.0 $mg.kg^{-1}$. Recently, in order to meet the European requirements, lower level of chloride content than 1.0 mg.kg^{-1} is needs to determine. The specified concentration range for the: reformate, virgin naphtha, aromatic hydrocarbons and hydrocarbon gaseous is 0.1 - 5 mg.kg^{-1} in Bulgaria, Lukoil-Neftochim Bourgas JSC.

The aim of this work is to optimize the analytical procedure parameters for determination of chloride compounds in the petroleum fractions and products by microcoulometric oxidative pyrolysis method in order to assure a proper detection and concentration limit and results with good accuracy and precision. Validation of the method including the optimized conditions developed was made.

2. Experimental

Apparatus

The determinations were performed with an Automatic analyzer microcoulometric titration system 120 Dohrmann, equipped with modules for automatic injection of liquid samples (Auto Sampler – CRI), automatic injection of gaseous samples (Gas/LPG) and automatic feeding of liquid and solid samples using a boat inlet (Auto Boat- SBI). Microcoulometric cell with electronic controller used for setting the operating parameters and integration of data was used for the titration.

Reagents

Analytical reagent grade chemicals (p. a. Merck and Fluka).were used. The stock standard solution had a chloride concentration 100 mg. L^{-1} and was prepared by dissolving chlorobenzene (minimum 99.9 % purity,) in isooctane. The calibration solutions were prepared by dilution of the stock standard solution and had concentrations in the range 0.05 – 10 mg. L^{-1} Cl.

Sampling and storing of the samples

Glass bottles with screw cap, sampling was performed for the liquid samples. Stainless steel bombs were used for the gaseous samples under pressure less than 500 psig. The solid samples were stored in glass containers with.

Preparation of apparatus and titration procedure

The instructions of the standard methods recommendations [4, 5] and manufacturer [6] were followed in the study for the procedure optimization.

3. Results and discussion

Optimizing the oxidative pyrolysis parameters

Optimization of the conditions for the oxidative pyrolysis is connected with the proper choice of the inlet and outlet temperatures of the pyrolysis furnace in order to convert completely the organic chlorides to hydrogen chloride (HCl). Solomon [7] considers that the conversion rate of the organic and inorganic bonded chloride increased with the temperature and has maximum value at 900°C. The grave problem in this process represents the erosion of the quartz tube. In the opinion of the Matsuzaki [8] the problem can be resolved by promoting of the oxidative process of the burning products with the help of CuO catalyst in the quartz tube outlet or by increasing of the inlet temperature. Practically, the recovery of HCl requires an individual approach to the specific organic matter and with a view to the apparatus design.

Experiments with an alteration of the inlet and outlet temperatures at constant pressure in the presence and without the catalyst CuO were performed. The maximum recovery of the chloride in the standard added and the precision of the results were the criterion for the optimization. These characteristics were satisfied at inlet temperature 850°C and the outlet temperature 950°C without using the catalyst.

Optimizing the parameters for selective titratable species formation

The major problem in the microcoulometric method is the formation of large water quantity in the burning process of the hydrocarbons, resulting in unsatisfactory precision of the titration, especially in the determination of low chloride content, whenever increase of the sample size is needed. The recommended from Van de Graats [9] excluding of the water by sulfuric acid washing in quartz scrubber is not recommend from the Dohrmann specialists. In their opinion the optimization of the sample injection rate and the polarization potential applied would be better resolution for increasing the recovery of the titratable species.

The availability of heavy metals, alkaline additions and sodium and magnesium salts in the samples has as a result incomplete burning. They overlay on the quartz tube surface or corrode it forming cankers. The titratable species formed may physical or chemical interacted with this matter or the corroded area and to decrease the chloride detectability. This problem can be resolved optimization the sample injection rate. On the other hand, the low rate is a cause for incorrect measurement of the registered very weak polarization current and the high rate results in formation of soot, which adsorb hydrogen chloride. These possible deflections are not in great importance in determination of chloride content above 1 $mg.kg^{-1}$, but are significant problem for levels below 1 $mg.kg^{-1}$. As it was established by experiments, the sample burning is complete and without soot formation when the sample injection rate was: 0.25 $\mu L.s^{-1}$ for liquid and gaseous samples; for the solid products it altered: from 0.1 $cm.s^{-1}$ in the inlet zone of the furnace to 0.02 $cm.s^{-1}$ in the hottest zone. The correlation factor achieved was in the range 0.8-1.2 within the permissible error, which was additional prove for proper burning.

Optimization of the polarization potential has significant importance for some level of the chloride. The lower values of this parameter provide high Ag^+ concentration and over titration of the hydrogen chloride transferred in the cell may be occurred. Conversely, higher values decrease the base Ag^+ concentration and increase the coulometric titration sensitivity, but provoke “tailing” of the peak registered due to the difficulty in measurement of the very weak polarization potential altering. The investigations with standard showed that the optimum polarization potential value for: chloride content from 1.0 to 10 $mg.L^{-1}$ is 250 mV and this one for chloride content less than 1.0 $mg.L^{-1}$ is 260 mV.

Optimization of the sample injection

The determination of the chloride contents less than 1.0 $mg.L^{-1}$ requires large sample volumes (40-50 μL) injected with a constant rate in order to avoid soot formation. This one can be achieve using auto-sampler SRI and auto-boat SBI. Additionally, in the automatic mode the signals integration is changed by measurement of the signal heights and the problem with the syringe damaging due to the high temperature, resulting in better accuracy. In order to assess the benefits of the automatic mode standard solution with 0.5 $mg.L^{-1}$ Cl were analyzed and the dependence potential/time for liquid samples were registered (Fig.1-3). As it is shown, in the automatic mode the sensitivity was increased and the base line was more stable.

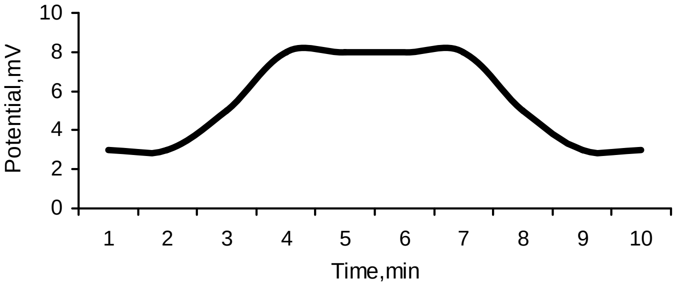

Figure 1. The dependence of the polarization potential from the time using auto- sampler SRI

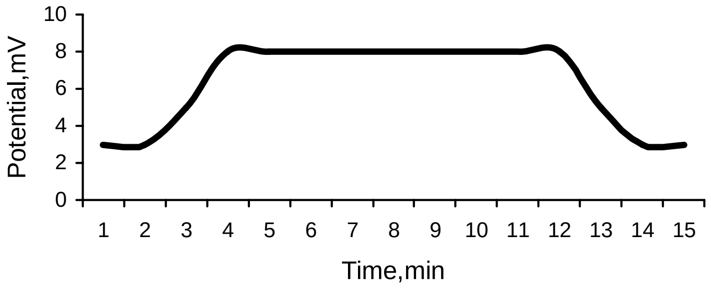

Figure 2. The dependence of the polarization potential from the time using auto- boat SBI

Negative interference was observed using the manual injection of the syringe (Fig.3), which provokes the results.

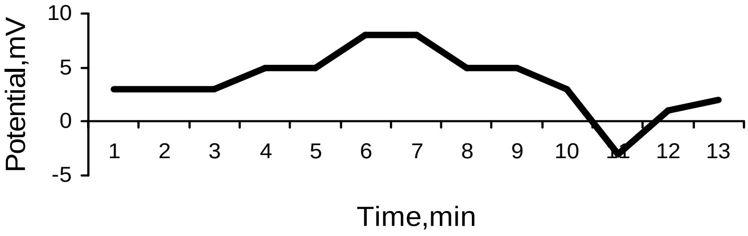

Figure 3. The dependence of the polarization potential from the time using manual injection

The accuracy of the determination of contents less than 1.0 $mg.L^{-1}Cl$, expressed as recovery of chloride in the standard, using the three injection modes is shown in Fig.4. The mode auto - boat ensures the nearest to 100% recovery. This benefit is probably due to the fact, that the platinum boat was at proper distance from the hot zone of the pyrolysis furnace and the possibility for increasing of the inlet temperature at 900°C can be used. At the same time a loss of volatile species was avoided.

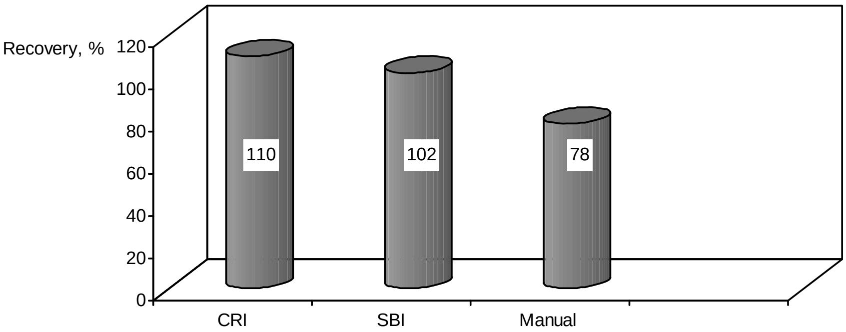

Figure 4. Recovery of chloride using three modes of sample injection

For the gaseous samples the proper conditions were a constant rate of injection using GAS/LPG module and sample sizes 5 or 25 μL in dependence of the chloride level.

The optimum parameters established for solid samples (polypropylene with chloride content from 23.8 to 44.2 mg.L^{-1}) injections using auto-boat SBI, ensuring the soot less sample burning were as follows:

Number of stop points: 3;

Parameters for the stop points:

	first	second	third
Stop position, mm	160	200	255
Stop time, s	180	300	480
Rate, cm.s^{-1}	0.1	0.01	0.02

Optimizing the calibration

It is well known, that the accuracy is best when the measured concentration is close to this one of the calibration standard. As the concentrations of the samples are thereabout known, the study was performed to assess the relative error of the determinations in dependence of the calibration standard used. The results are presented in Fig. 5. Seven standards (0.1; 0.2; 0.5; 1.0; 2.0; 5.0 and 100 mg.L^{-1} Cl) were measured like samples and its concentration was calculated using calibrations with the four individual standards: 1 – 0.5 mg.L^{-1} Cl; 2 – 1.0 mg.L^{-1} Cl; 3 – 5.0 mg.L^{-1} Cl; 4 – 100 mg.L^{-1} Cl. The relative errors of the calculated in this way sample concentrations were established. As it is shown in the figure, to attain the relative error ≤ 10 % the calibration standard for the measured concentrations from 0.1 to 2.0 mg.L^{-1} Cl should be 0.5 or 1.0 mg.L^{-1} Cl ; the calibration standard 5.0 mg.L^{-1} Cl is suitable for measured concentrations ≥ 1.0 mg.L^{-1} Cl and no higher than 5.0 mg.L^{-1} Cl. Relative error of 4 % might be assured for the lower concentration (0.1 – 0.5 mg.L^{-1} Cl) if the calibration standard has a concentration up to 0.5 mg.L^{-1} Cl.

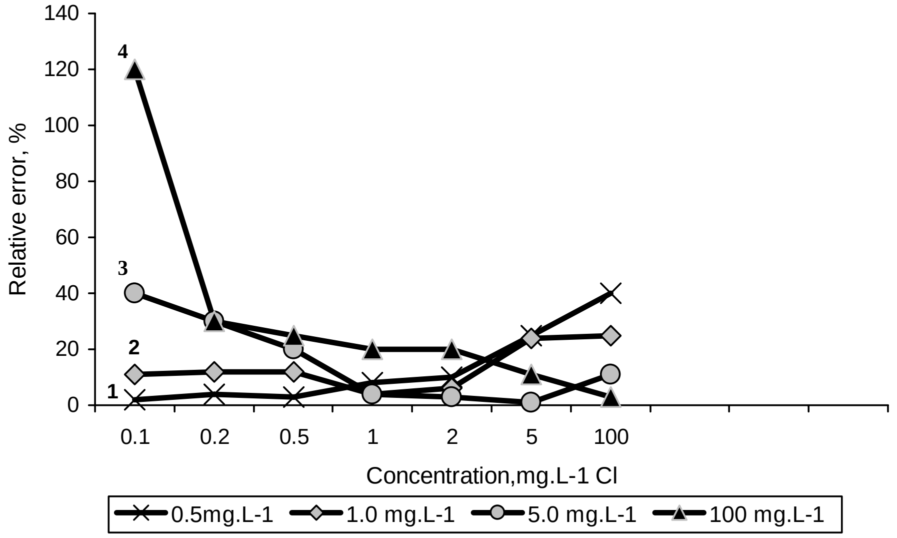

Figure 5. The relative error of the measurements in dependence of the calibration standard used

Because the accuracy is related to the solvent used for the calibration standard: isooctan, reformate and toluene were used in the study. Isooctan imitates the gasoline matrix and had chloride content, less that 0.2 mg.L^{-1}. The reformate and toluene imitate the aromatic matrix and have the same content of chloride. The analytical characteristics established using these solvents (Table I) were similar for isooctan and reformate, the recovery using toluene was to a certain extent increased. Therefore, isooctan was recommended as calibration solvent in analysis of gasoline fractions, gaseous hydrocarbons and polymeric products and reformate was useful for the analysis of the aromatic hydrocarbons with chloride content less than 1.0 mg.L^{-1}.

Table I. Analytical characteristics of the determinations using different calibration solvents

Analytical characteristics	**Isooctan**	**Toluene**	**Reformate**
Relative standard deviation, %	5.5	6.0	2.3
Detection limit, mg.L^{-1}	0.09	0.16	0.04
Recovery, %	96	113	96

Validation of the optimized procedure

The accuracy for liquid and polymeric products was assessed using chlorobenzene in isooctan spikes and was expressed as “added/obtained” (Fig. 6 and 7).

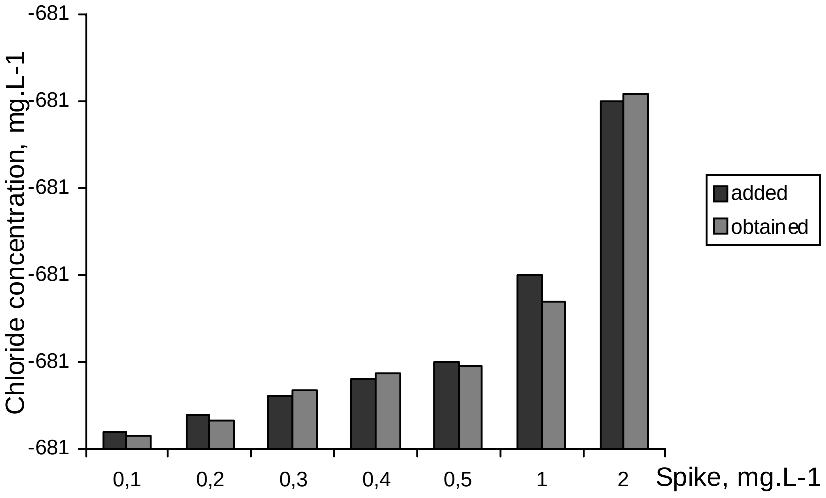

Figure 6. Spike recovered (liquid products)

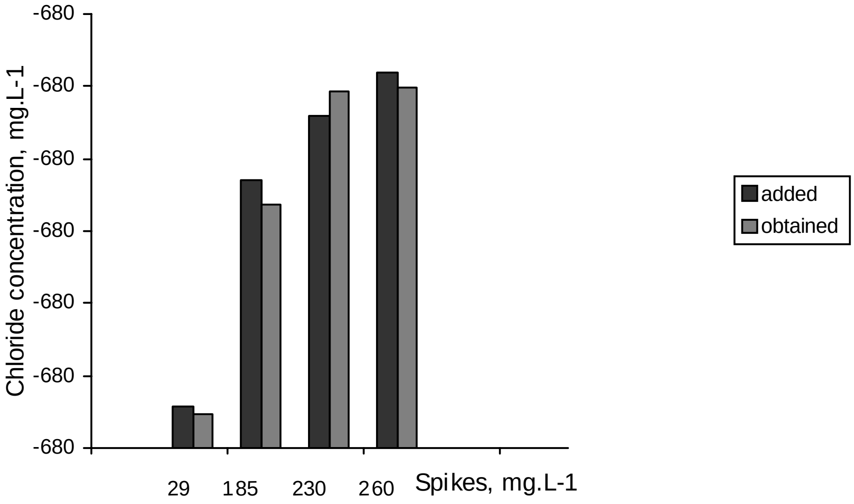

Figure 7. Spike recovered (polymeric products)

The accuracy as recovery of spikes (R, %) and precision expressed as relative standard deviation (RSD, %) was evaluated analyzing hydrogenated gasoline fractions, industrial aromatic hydrocarbons, polypropylene, propylene and propane-butane fraction (Table II). The detection limits were calculated on the base of triple standard deviation of the chloride determination in the samples (Table II). The relative combined uncertainties U_c (mg.L^{-1}) were calculated using the follow expression:

$$U_c = k\ (0, 95).\ S / \sqrt{n} \qquad (1)$$

Where: k = 2 (close to 95 % confidence level);

S - standard deviation from a limited number of measurements (n).

The relative uncertainties U_c (%), shown in Table II, were calculated using the follow expression:

$$U\ (\%) = U_c.\ 100 / C \qquad (2)$$

Where: C – the chloride content of the sample, (mg.L^{-1}).

Table II. Analytical characteristics of the microcoulometric method

Sample	**Cl content, mg. L^{-1}**	**Mean RSD, %**	**Mean R, %**	**DL, mg.L^{-1}**	**Uc, %**
Liquid petroleum products	Up to 0.5	4.7	99.7	0.06	5.3
Liquid petroleum products	≥ 1.0	3.5	93.0	0.15	3.8
Aromatic hydrocarbons	≤ 1.0	7.7	94.0	0.07	8.0
Polypropylene	≥ 1.0	2.1	98.0	1.2	2.5
Propylene, Propane-butane	≤ 1.0	6.1	-	0.09	3.8

The improved method was validated for chloride content determination in: benzene, toluene, xylenes, ethylbenzene, hydrogenate, reformate, virgin naphta, propylene, propane-butane fraction. A comparison between the microcoulometric oxidative pyrolysis method and a spectrophotometric method (ASTM 2384 [10]) used after burning the samples by the Wickbold apparatus was made (Table III). The bias was not considerable.

Table III. Comparative data for the microcoulometric and spectrophotometric methods

Sample	**Chloride content determined, mg.L^{-1}**	
	Microcoulometry	**Spectrophotometry**
Hydrogenate	0.3	Less than DL (0.5)
Virgin naphta	1.9	2.4
Propylene	0.2	Less than DL (0.5)
Polypropylene	29.0	27.0

4. Conclusion

Improved characteristics for the determination of chloride compounds in petroleum products are achieved optimizing the procedure for the oxidative pyrolysis and the microcoulometric titration and using automatic injection of the gaseous, liquid and solid samples. The method is validated and is applicable for samples with chloride content less than 1.0 mg.L^{-1}.

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