

THE INFLUENCE OF SAMPLE pH ON THE DETERMINATION OF SELECTED CARBOXYLIC ACIDS BY ISOCRATIC ION CHROMATOGRAPHY

Paulina Pecyna-Utylska¹, Tomasz Konieczny¹, Rajmund Michalski¹, ✉

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Abstract. Validated isocratic ion chromatography method with suppressed conductivity detection has been developed for the simultaneously determination of common inorganic anions (F^- , Cl^- , NO_3^- , PO_4^{3-} , SO_4^{2-}), as well as formate and acetate. Liquid samples originate from absorption of gaseous by-products from coal combustion with and without the addition of medium-density fireboards. The influence of sample pH changes on carboxylic acids determination has been tested.

Keywords: coal combustion, furniture waste, carboxylic acids, ion chromatography.

1. Introduction

In Eastern Europe countries, such as Poland and Ukraine, hard coal and lignite still remain the main source of energy production. These countries have extensive mining industries, contributing significantly to the total amount of industrial wastes generated in the country. The problem is not only coal burning in industrial installations, but so-called low emissions caused by its use for heating private homes. Because of economic reasons and a lack of ecological awareness, the worst quality coal is often burned, including various additives such as furniture waste or even plastic. This problem is still growing and requires intervention at governmental and international levels. Officials are focused on the contributions of home heating, known as low-stack emissions, which are severe and very visible. Anyway, millions of people burn coal, often the cheapest, most polluting grades, in old furnaces with poor filters. In addition, they often do not maintain proper coal combustion parameters, which may contribute to the formation of large amounts of pollution. A very interesting example work on that topic is article of Małkowski and Tymoshenko devoted to the quality of

coal in Poland, Russia and Ukraine and its effect on dust emission into the atmosphere during combustion [1].

The health consequences are severe. According to new regulations a large part of furnaces will be replaced with a connection to the district heating network, which is powered from the power plant. Anyway, the main fuel burned in the power plant is coal. The difference, however, lies in the fact that it is easier to monitor emissions from one plant than from the tens of thousands of chimneys. In addition, the power plants are subject to routine and special safety reviews. Substituting coal with biomass (*e.g.* through international trade in wood pellets) could seriously damage carbon stocks in global forests, thereby accelerating rather than slowing global warming [2].

Already in the 1960s, it was found that not only sulfur and nitrogen oxides, but also carbonyl compounds, (*i.e.* low carboxylic acids) origin from the combustion of various fuels play an important role in the formation of acid rains [3]. Moreover, important sources of carboxylic acids in the environment include plant vegetation and microbiological activity [4]. Many carboxylic acids occur naturally (*e.g.* oxalic, formic, or citric acids). Some of them are commonly used in various industries. Due to the broad range of their applications, carboxylic acids and their derivatives are present in different elements of the environment, including air (gaseous phase, aerosols, solid particles, ice, snow, rain), different types of water (surface and ground water, drinking water), and solid samples (soil, food, medicines, plants, *etc.*).

Considering the above, fast and reliable methods for carboxylic acids analyses at low concentration levels are necessary. Various analytical methods and techniques, both manual and instrumental, such as spectrophotometric, enzymatic, chromatographic and the ones based on capillary electrophoresis can be used for ions analysis, including organic acids. Ion chromatography and related techniques are particularly useful for anions and cations analyses [5, 6]. Anion-exchange chromatography and ion exclusion chromatography are currently the most popular instrumental methods in that range of applications [7]. Their most important advantages are: the possibility of

¹ Institute of Environmental Engineering,
Polish Academy of Sciences,
34, Skłodowska-Curie Str., Zabrze, Poland
✉ rajmund.michalski@ipis.zabrze.pl

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simultaneous determination of several ions in a short time; a small amount of sample needed for analysis; the possibility of using various detection modes; possibility of simultaneous determination of organic and inorganic ions; high separation selectivity; speciation analysis; as well as safety and relatively low operating costs. The most versatile are hyphenated techniques that combine the advantages of separation methods with spectroscopic ones, such as IC-MS and IC-ICP-MS [8], especially in the range of speciation analysis [9]. The parameters influenced on ions separation efficiency in ion chromatography are: the type of stationary phases use; mobile phase type, concentration, flow rate and pH; applied detection mode; and sample preparation methods [10]. Low molecular weight carboxylic acids, such as acetic and formic elute between F^- and Cl^- anions. Due to their similar retention times, it is not easy to separate them under isocratic conditions on typical anion exchange columns. This concerns especially real samples with complex matrices. The lowering of eluent concentration or its flow rate may improve the peaks resolutions, but this will increase the total time of analysis. One of the simplest options when optimizing the separation processes in ion chromatography is changing the concentration, pH and flow rate of applied eluents. Given that carboxylic acids dissociation strongly depends on sample pH, when they are analyzed in low pH, they may not be detected, or their concentrations would be underestimated.

The aim of the research was development and optimization the isocratic ion chromatography method with suppressed conductivity detection for the simultaneously determination of common inorganic anions (F^- , Cl^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) and formate, acetate and oxalate. The second aim was to test how the changes of pH values of samples influence the reliable determination of simply carboxylic acids. The developed method was used for the determination of selected carboxylic acids in samples obtained by absorption of gaseous by-products of coal combustion with and without the addition of medium-density fireboards (MDF).

2. Experimental

2.1. Standards and Reagents

All reagents used were of analytical grade. Standard solutions of formate, acetate and oxalate were prepared by appropriate dilution of their stock solutions (1000 ± 5 mg/l each, standards for IC, Sigma Aldrich, USA) in Milli-Q-Gradient ultrapure deionized water (Millipore, Merck). Calibration solutions were prepared by dilution of a standard solution. The mobile phase consisted of 4.5 mM Na_2CO_3 and 1.4 mM $NaHCO_3$ was

prepared by dissolving appropriate amounts of Na_2CO_3 and $NaHCO_3$ powders (SPC Science AccuSPEC, ACS Grade, France) in Milli-Q-Gradient degassed ultrapure deionized water (Millipore, Merck).

Five standard solutions with nominal values: 1.675, 4.0, 6.8, 9.225 and 12.0 (Reagecon, Ireland) were used to calibrate the pH-metric electrode. In order to calibrate the conductivity sensor, standard solution from Reagecon (Ireland) with nominal value of 1413 $\mu S/cm$ was used.

2.2. Samples

Three types of fuels in two repetitions were combusted in a laboratory-scale burner. In Table 1 the list of samples is reported.

The most important physical and chemical parameters of the fuels used are given in Table 2.

Table 1

List of analyzed samples

Sample number	Type of sample
1	Coal, first series
2	Coal, second series
3	Coal + MDF (ratio 1/1, w/w), first series
4	Coal + MDF (ratio 1/1, w/w), second series
5	Coal + MDF (ratio 9/1, w/w), first series
6	Coal + MDF (ratio 9/1, w/w), second series

Table 2

Physico-chemical properties of coal and MDF (analytical state)

Property	Coal	MDF
Ash content, %	3.69	0.92
Carbon content, %	73.19	49.01
Hydrogen content, %	4.65	6.36
Sulphur content, %	0.56	<0.03
Moisture, %	6.63	4.68
Lower heating value, kJ/kg	27390	16970
Higher heating value, kJ/kg	28390	18350

2.3. Sampling and Sample Preparation

The process of coal combustion and co-incineration of coal with or without MDF fireboard in two mass ratios (coal/MDF: 1/1 and 9/1) was carried out in a laboratory-scale installation at the Institute of Environmental Engineering, Polish Academy of Sciences in Zabrze (Poland). The scrubbers contained ultrapure deionized water (pH = 5.61 and electrolytic conductivity <0.054 $\mu S/cm$). The experiments were conducted for two series for each analyzed fuel. Liquids samples from

scrubbers after absorption of gaseous by-products from combustion process were divided into two parts. In the first one pH and conductivity were determined. The second part of absorption solutions were filtered through a 0.22 µm PVDF syringe filter. Then, the pHs of samples were adjusted to the range of 10–10.5 (v/v) with the mixture of 45 mM Na₂CO₂ + 14 mM NaHCO₃ (10x concentrated eluent). Next, in both samples types (original and with modified pH) inorganic anions (F⁻, Cl⁻, NO₃⁻, PO₄³⁻, SO₄²⁻) and formate, acetate and oxalate ions were analyzed by using developed isocratic ion chromatography method. All samples were stored at 277 K before analyses.

2.4. Apparatus and Analytical Conditions

The pH was determined using the inoLab IDS Multi 9310 device with pH-metric electrode IDT SenTix® 940 (WTW, Poland) according to EN ISO 10523:2012 standard. The conductivity was measured using inoLab IDS Multi 9310 device using conductometric sensor TetraCon 925 IDS (WTW, Poland) according to EN 27888:1999 standard. Simultaneous separation and determination of inorganic and organic anions was carried out on Dionex ICS-1100 (Thermo Scientific, USA) ion chromatograph equipped with conductivity detector and isocratic pump. Instrument control, construction of calibration curves, peak analysis and data acquisition were achieved with the Chromeleon software. Separation conditions are reported in Table 3.

Table 3

Analytical conditions for the analysis of anions

Parameter	Value
Analytical Column	Dionex IonPac AS22 (4×250 mm)
Guard column	Dionex IonPac AG22 (4×50 mm)
Elution mode	Isocratic
Eluent	4.5 mM Na ₂ CO ₃ + 1.4 mM NaHCO ₃
Eluent flow rate	1.2 ml/min
Detection	Suppressed conductivity
Temperature	303 K
Injection volume	100 µl

2.5. Calculations and Validation of Ion Chromatography Method

Repeatability was calculated for concentrations of acetate and formate in real samples after seven replicate injections of every sample within one analytical run. The method repeatability was expressed by coefficient of variation. Limits of detection and limits of quantification were calculated from calibration curves of formate and acetate and were based on the following dependences:

$$LOD = \frac{3.3S_d}{b} \tag{1}$$

$$LOQ = \frac{10S_d}{b} \tag{2}$$

where *LOD* is a limit of detection; *LOQ* is a limit of quantification; *S_d* is a standard deviation value; *b* is the slope of the calibration curve.

The standard deviation values were determined as a standard deviation for 10 times analysis of the standard solutions at the concentrations of 15, 50 and 60 µg/l for formate, acetate, and oxalate, respectively. The recovery was determined with measurements of the real samples spiked with known amounts of formate, acetate and oxalate standard solutions. Selected method validation parameters are presented in Table 4.

The Pearson's correlation parameter was used to determine the relationship between the sample pH and sample conductivity values. Change scores of formate and acetate concentrations before and after pH adjustment were compared using a dependent *t*-test for both original and modified samples (two-tailed, α = 0.05).

3. Results and Discussion

Real liquid samples were analyzed in the range of:

- pH and conductivity values of original and modified samples (Fig. 1),
- concentration of acetate, formate and oxalate in original and samples after pH adjustment.

Table 4

Selected method validation parameters for carboxylic acids

Ion	Relative standard deviation of repeatability, %	<i>LOD</i> , µg/l	<i>LOQ</i> , µg/l	Recovery, %
Formate	10.2	5.51	16.7	91.6 ± 11.7
Acetate	12.9	9.99	30.3	91.5 ± 10.3
Oxalate	12.7	17.2	52.1	90.6 ± 4.33

It was noticed that pH and conductivity values of samples from scrubbers depend on the type, composition and mass ratios of the components of the applied fuels. Differences between pH and conductivity values for liquid samples from scrubber and the absorbent solution (deionized water) were observed. The scrubber liquids pH values ranged between 3.00 and 4.34, and conductivity values were between 54.2 and 409 $\mu\text{S}/\text{cm}$. The highest pH value was found in liquid from scrubbers after co-incineration process of coal with MDF in mass ratio 1:1 (second series), and the lowest one was in samples from scrubber after coal combustion (first series). The highest conductivity value was measured in liquid from scrubbers after coal combustion (first series), and the lowest one was in scrubber liquid after co-incineration of coal with MDF in mass ratio 1:1 (second series). A relationship was observed between the pH and conductivity values: the

lower the sample pH, the greater the conductivity of the sample (Pearson correlation was strong $r = -0.975$, $\alpha = 0.001$).

In acid samples they are poorly dissociated, but the degree of dissociation increases with increasing solution pH value. Thus, a portion of 10 x concentrated eluent was added to filtered sample (1/10, v/v) to change pH from around 3 up to 10. It results in increasing the dissociation rate of analyzed carboxylic acids. The obtained results (after pH value adjustment) are shown in Fig. 2.

The obtained results confirm that sample pH value strongly affects determined concentration of acetate and formate in scrubber liquids. The results of determinations of formic and acetic acid in samples with and without pH value adjustment are shown in Figs. 3 and 4, respectively. Concentrations of oxalate in samples were below the limit of quantification.

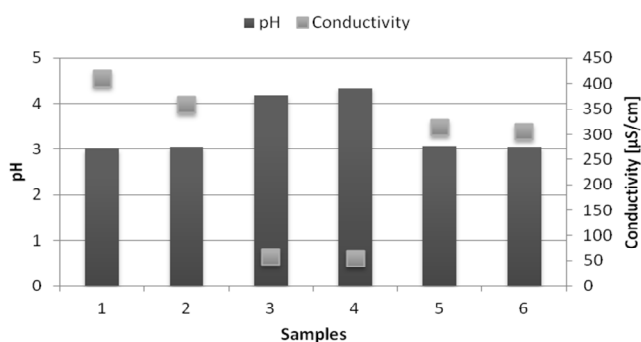


Fig. 1. pH and conductivity values of original samples

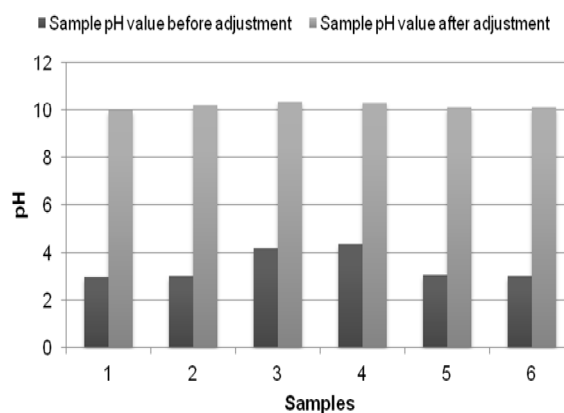


Fig. 2. Sample pH value before and after adjustment

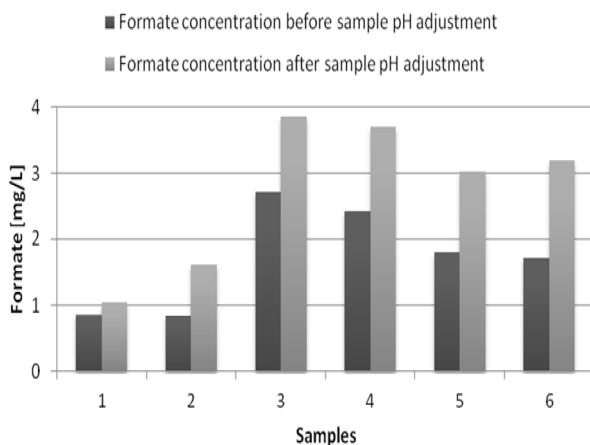


Fig. 3. Comparison of formate concentration in samples before and after sample pH adjustment

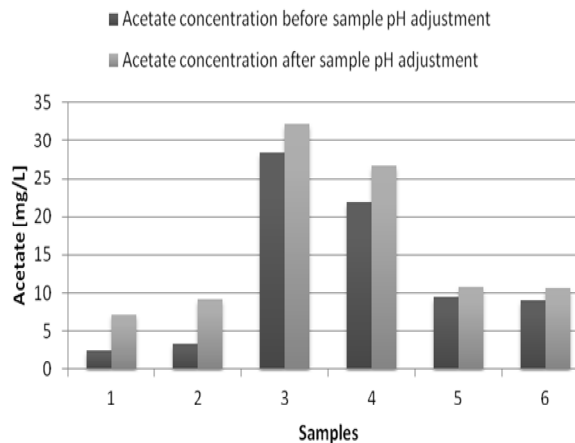


Fig. 4. Comparison of acetate concentration in samples before and after sample pH adjustment

4. Conclusions

Burning of low-quality coal in improper conditions, especially with various additives, including furniture waste poses a very serious threat to the environment and human health, due to by-products formation, which are not regularly monitored. These include also carboxylic acids, which should be determined at low concentration levels by using suitable analytical method.

Specific conclusions from conducted research are as follows:

- Isocratic ion chromatography with suppressed conductometric detection for simultaneous separation and determination of formic and acetic acids as well as the main inorganic anions was developed and validated.

- In acidic samples carboxylic acids were not completely dissociated. The dissociation of carboxylic acids is pH-dependent process, thus concentration of analyzed acids in sample should be modified by changing the pH of the sample. Correction of the sample pH (increasing the pH of the sample from 3 to 10 by using of a 10-fold concentrated $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ eluent) causes increase in the degree of dissociation of carboxylic acids, which significantly improves the limits of quantification.

- This aspect of sample preparation should not be skipped during reliable carboxylic acid analyses in real samples.

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ВПЛИВ pH ЗРАЗКА НА ВИЗНАЧЕННЯ КАРБОНОВИХ КИСЛОТ ІЗОКРАТИЧНОЮ ЙОННОЮ ХРОМАТОГРАФІЄЮ

Анотація. Розроблено і перевірено метод ізократичної йонної хроматографії з детектором пригніченої провідності для одночасного визначення загальних неорганічних аніонів (F^- , Cl^- , NO_3^- , PO_4^{3-} , SO_4^{2-}), а також форміату та ацетату. Після поглинання газоподібних побічних продуктів при спалюванні вугілля з додаванням ламінату середньої щільності та без нього отримані рідкі зразки. Встановлено вплив зміни pH зразка на визначення карбонових кислот.

Ключові слова: спалювання вугілля, відходи виробництва меблів, карбонові кислоти, йонна хроматографія.