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Determination of water-soluble forms of oxalic and formic acids in soils by ion chromatography

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Abstract. Carboxylic acids (CA) play an important role in the chemical composition origin of soils and migration of elements. The content of these acids and their salts is one of the important characteristics for agrochemical, ecological, ameliorative and hygienic assessment of soils. The aim of the article is to determine water-soluble forms of same carboxylic acids – (oxalic and formic acids) in soils by ion chromatography with gradient elution. For the separation and determination of water-soluble carboxylic acids we used reagent-free gradient elution ion-exchange chromatography ICS-2000 (Dionex, USA), the model solutions of oxalate and formate ions, and leachates from soils of the Kola Peninsula.

The optimal gradient program was established for separation and detection of oxalate and formate ions in water solutions by ion chromatography. A stability indicating method was developed for the simultaneous determination of water-soluble organic acids in soils. The method has shown high detection limits such as 0.03 mg/L for oxalate ion and 0.02 mg/L for formate ion. High signal reproducibility was achieved in wide range of intensities which correspond to the following ion concentrations: from 0.04 mg/g to 10 mg/L (formate), from 0.1 mg/g to 25 mg/L (oxalate). The concentration of formate and oxalate ions in soil samples is from 0.04 to 0.9 mg/L and 0.45 to17 mg/L respectively.

1. Introduction

Carboxylic acids (CA) play an important role in the chemical composition origin of soils and migration of elements [1]. The content of these acids and their salts is one of the important characteristics for agrochemical, ecological, ameliorative and hygienic assessment of soils [2-4]. According to the modern notions oxalic acid is a harmful substance that is naturally present in various foodstuff [5-6]. It is characterized by demineralizing factors that inhibit the uptake of Ca^{+2}, Fe^{+2}, Zn^{+2} and some other elements due to the formation of sparingly soluble compounds [7-8].

Identification of individual carboxylic acids remains quite challenging due to the low concentrations of these compounds in natural water and soils and their physicochemical properties. Carboxylic acids are unstable compounds which easily undergo degradation during sample preparation, such as extraction or concentration [9-10]. Gas chromatography, mass spectrometry and ion chromatography are still the most common methods to determine the carboxylic acids. Ion chromatography (IC) as the most preferred method of analysis has been widespread in recent years due to relatively simple equipment, the most effortless sample preparation, and the use of different modes of operation, such as gradient elution [11-12].

The aim of the article is to determine water-soluble forms of same carboxylic acids – (oxalic and formic acids) in soils by ion chromatography with gradient elution.

2. Methods

To separate and determine water-soluble carboxylic acids we used reagent-free gradient elution ion-exchange chromatography ICS-2000 (Dionex, USA) with conductivity detection, equipped with vacuum degas, carbonate removal device CRD 200 (Thermo Scientific, USA), a separating column 2*50 mm IonPac AG 20 (Thermo Scientific, USA), background eluent conductivity suppressor ASRS 300 (2 mm) (Dionex, USA) and Dionex EGC III KOH Potassium Hydroxide Eluent Generator Cartridge. The eluent was delivered at a flow rate of 0.25 ml/min, injected sample volume was 1 ml Instrument control and data processing was performed using Chromeleon software.

The model solutions of oxalate and formate ions were prepared using the corresponding standards (Oxalate Standard, Fluka Analytical, USA, c=1 mg/ml and SSRS 7278-96, Ekmets, Russia) and deionized water (Simplicity, Millipore, USA). The concentration of oxalate and formate ions in the model solutions is 10 mg/L. Calibration solutions (0.01 to 10 mg/L) were prepared by serial dilution of a standard solution just before analysis.

The distribution of oxalate and formate ions was studied in soil samples collected from five sites in the study area, which was the Imandra lake surrounding area (the Kola Peninsula). Samples were taken from various depths. The scheme of soil sample preparation for analysis is shown in Figure 1. According to the scheme, one part of each soil sample was mixed with 5 parts of distilled water. After 24 h, the pH was measured and the samples filtered through a 0.45 μm cellulose nitrate filter.

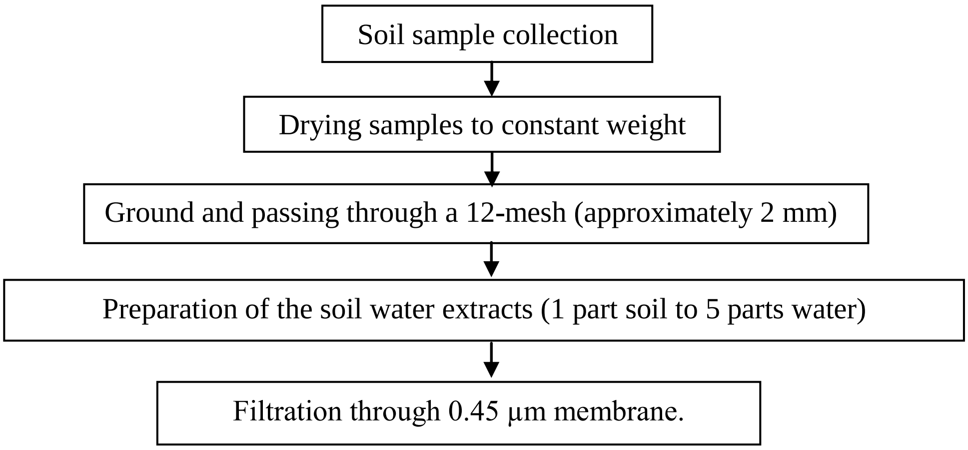

Figure 1. Scheme of soil sample preparation for analysis.

3. Results and discussion

The conditions for separation of oxalate and formate ions were optimized to obtain reproducible measurements of analytical signal. Optimized gradient program was established and presented in Figure 2.

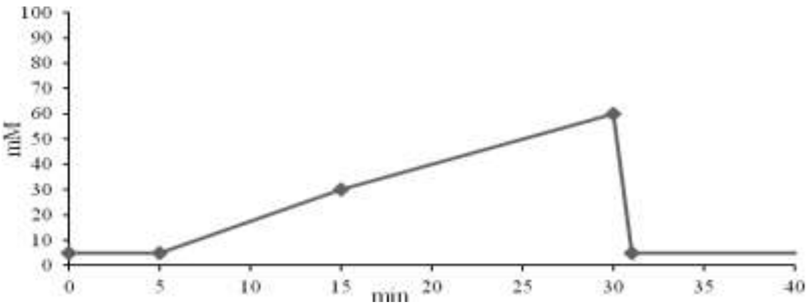

Figure 2. Multi-Step Gradient for carboxylic asid separation.

As shown in Figure 2, separation starts with a weak eluent. Either initially or as soon as the most weakly adsorbed components are eluted, ionic concentration of the eluent starts slowly increasing, and by the end of the separation reaches some maximum value, enough to elute quickly the most strongly adsorbed components. Thus, each component of mixture is fully separated at the optimum eluent composition for shorter period than in isocratic mode.

To establish the retention times for both anions, the model solutions of oxalate and formate ions were analysed. The retention time was experimentally determined that was 16.9±0.1 min and 7.6±0.1 min for oxalate and formate ions respectively (Figure 3).

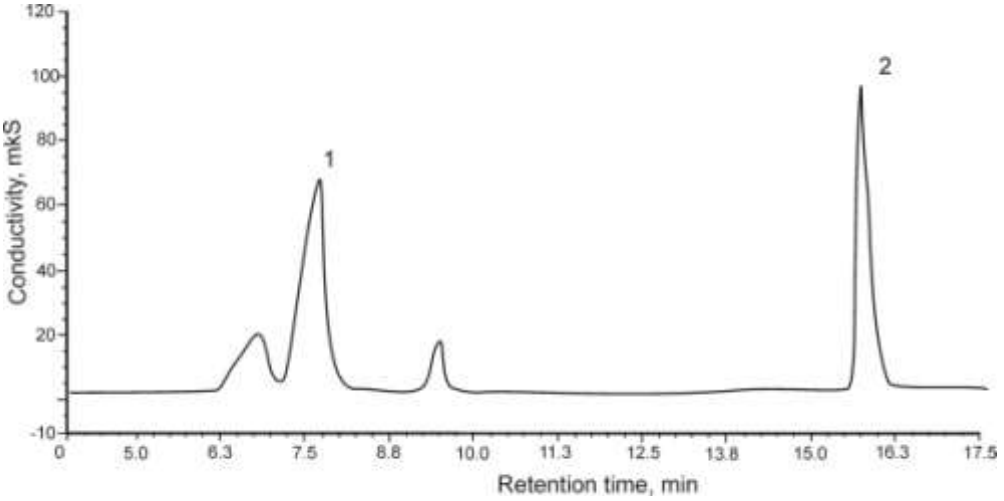

Figure 3. Ion chromatogram of the model solutions of oxalate and formate ions.

The basic metrological characteristics of oxalate and formate ion determination water solution are presented in Table 1. The concentrations of carboxylic acid ions were determined based on previously created calibration curve.

Table 1. Basic metrological characteristics of oxalate and formate ion determination by ion chromatography (n = 3; P = 0.95).

Element	Retention time, min	Detection limit, mg/L	Linear range*, mg/L
$HCOO^-$	7.6±0.1	0.02	0.04 – 10
$C_2O_4^{-2}$	16.9±0.1	0.03	0.10 – 25

*- dilution factor is unaccounted for

Based on the results of model solution research, the distribution of water soluble form of carboxylic acids in soil of the Kola Peninsula was found. The results of the determination of oxalate and formate ions are shown in Table 2.

The concentration of formate and oxalate ions in soil samples ranges from 0.04 to 0.9 mg/L and from 0.45 to 17 mg/L respectively. Thus, the content of water-soluble formic acid form in the studied soils is significantly lower than that of oxalic acid.

Table 2. Determination of formate and oxalate ions in leachates of the soils of the Kola Peninsula (n = 2; P = 0.95).

Samples	pH	Concentration, mg/L	
		$HCOO^{-}$	$C_2O_4^{-2}$
1	5.1	0.29±0.01	0.45±0.02
2	5.2	0.040±0.002	0.52±0.02
3	6.4	0.38±0.01	1.1±0.04
4	4.9	0.30±0.01	5.90±0.18
5	4.5	0.93±0.04	17.00±0.51

The method of standard addition was applied to confirm analytical validity of oxalate and formate ion determination in the leachates of the soils by ion chromatography. To the studied soil leachates, the addition was made in quantity equal to the initial concentration of ion in the samples. The results are shown in Table 3.

Table 3. Validation of results (n = 3; P = 0.95).

Sample	pH	Concentration, mg/L					
		$HCOO^{-}$			$C_2O_4^{-2}$		
		Sample	Standard	Total concentration	Sample	Standard	Total concentration
1	5.1	0.29±0.01	0.20	0.45±0.02	0.45±0.02	0.50	0.94±0.05
2	5.2	0.040±0.002	0.05	0.090±0.005	0.52±0.02	0.50	1.00±0.05
3	6.4	0.38±0.01	0.20	0.55±0.02	1.1±0.04	1.0	2.00±0.08
4	4.9	0.30±0.01	0.30	0.60±0.02	5.90±0.18	5.0	11.0±0.55
5	4.5	0.93±0.04	1.0	1.90±0.04	17.00±0.51	15	32.0±1.6

The present results show that statistically significant systematic errors are not identified while determining formate and oxalate ions by the developed technique.

4. Conclusions

1. The optimal gradient elution mode has been found to determine oxalate and formate ions in aqueous solutions.
2. A stability indicating method was developed to determine simultaneously water-soluble form of carboxylic acids in soils. The method has shown high detection limits such as 0.03 mg/L for oxalate ion and 0.02 mg/L for formate. High signal reproducibility was achieved in wide range of intensities which correspond to the following ion concentrations: from 0.04 mg/L to 10 mg/L (formate), from 0.1 mg/L to 25 mg/L (oxalate).
3. The accuracy of the obtained results is confirmed by the method of standard addition.
4. The concentration of formate and oxalate ions in soil samples ranges from 0.04 to 0.9 mg/L and from 0.45 to 17 mg/L respectively. Thus, the content of water-soluble formic acid form in the studied soils is significantly lower than that of oxalic acid.

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