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Determination of inorganic ions in carboxylic acids by ion chromatography[☆]

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ABSTRACT

A method has been developed for the quantitative determination of various inorganic impurities present in carboxylic acids. The spiked as well as unspiked analytes were subjected to oxidative UV photolysis prior to ion chromatographic analysis. This procedure has definite advantages compared with other sample pretreatment methods: it is a simple procedure and the reagent requirement is minimal. Inorganic cations and anions, except nitrite, nitrate, iodine, sulphite and manganese(II), are unaffected by UV radiation. Depending upon the nature of impurity to be analysed and the amount of carboxylic acid, the UV photolysis time can be adjusted as required. The method was tested on several aliphatic as well as aromatic acids and found to be satisfactory for the determination of chloride, bromide, phosphate, sulphate, iron(III), lead(II), copper(II), zinc(II), nickel(II) and cobalt(II). Detection limits of the proposed method are between 5 and 25 ng/ml and calibration curves were found to be linear up to 1–2 μg/ml.

INTRODUCTION

Carboxylic acids play a vital role in the modern industrial world and find numerous applications. They are widely used in the food, pharmaceutical and electronics industries. The determination of trace inorganic constituents in carboxylic acids is desirable in a number of industrial processes, as in many industries the requirements for lower impurity levels are exceeding the limits of current analytical methods.

In many instances, new specifications are being set with impurities at μg/l levels.

The determination of trace inorganic impurities in organic matrices including carboxylic acid is generally based on classical analytical techniques such as volumetric and gravimetric analysis and/or turbidimetry and colorimetry [1]. These techniques require sample preparation aimed at destroying the organic matrix, which is usually done by dry ashing, involving complete destruction of all organic matter at very high temperatures, or by wet digestion with mixed acids.

Ion chromatography is a well-established and quite sensitive technique for the simultaneous determination of many ionic impurities in various matrices [2,3], as it is flexible in terms of operation and optimization. However, in many cases this technique, too, needs to be sup-

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plemented with sample pretreatment to overcome the problems related to matrix interferences.

PRELIMINARY STUDIES

The chromatographic behaviour of many carboxylic acids was examined using an AS9 anion separator column and different eluents containing varying proportions of sodium carbonate and sodium hydrogencarbonate at different flowrates. Many carboxylate ions were found to have retention times close to those of the inorganic anions to be analysed as impurities, i.e., chloride, bromide, nitrite, nitrate, phosphate, arsenate, sulphite and sulphate. In most cases it was found that the large peak due to the carboxylate ion masked the smaller peaks due to the spiked inorganic impurity anions. Attempts to analyse the cationic impurities, viz., lead, copper, iron, manganese, cobalt, zinc and nickel, without sample pretreatment also failed, as most of the carboxylate ions formed complexes with the metals, thereby making their quantitation almost impossible. In order to reduce the matrix effect, the dilution of the matrix was not preferred, because this led to the dilution of the impurities to below the detection limits for the various ions under investigation. It was therefore necessary to modify the sample in a manner that avoids dilution and permits quantitation without interferences resulting from the matrix. For this purpose UV photolysis of carboxylic acids was utilized as it is quite effective for the destruction of the organic matrix, without affecting most of the inorganic ions.

UV photolysis optimization

A 50-mg aliquot of each carboxylic acid sample was mixed with 1 ml of H_2O_2 (30%) and subjected to UV photolysis at $85 \pm 5°C$. Later, it was cooled, diluted to 5 ml and analysed by ion chromatography. It was found that the photolysis time for the destruction of the carboxylic acid depend upon the quantity and the nature/type of the acid. In most cases 2 h of UV photolysis was sufficient for the complete decarboxylation/destruction of the matrix. The carboxylic acids, having a strong electron-attracting group (–I

substituent, where I = inductive effect) on the α-carbon atom, were decarboxylated in less time. On the other hand, decarboxylation of formic and acetic acid required much time, because in the presence of hydrogen peroxide these acids form stable peroxy acids and thus prevent the formation of free ·OH radicals. The findings related to the decarboxylation and UV photolysis time are summarized in Table I.

To make the present sample pretreatment amenable for the widest range of applications, the procedure was optimized by making investigations with "synthetic solution 1", comprising 1000 mg/l each of formic, acetic, lactic, citric, tartaric, oxalic, malonic, succinic, fumaric, benzoic, phenylacetic, phthalic and salicylic acids. A 1-ml volume of "synthetic solution 1" was subjected to UV photolysis in the presence of hydrogen peroxide, as described earlier. Investigations revealed that 1 ml of this solution requires 1 ml of hydrogen peroxide for the complete disappearance of all the peaks due to carboxylate ions in 2 h, thus permitting the determination of inorganic anions. However, the

TABLE I

PHOTOLYSIS TIME FOR DECARBOXYLATION OF DIFFERENT AMOUNTS OF ACIDS

Acid	Photolysis time for complete destruction (min)		
	50 mg	100 mg	200 mg
Formic	100	120	150
Acetic	200	240	360
Propanoic	80	110	125
Butyric	80	120	125
Benzoic	60	60	60
Lactic	60	75	90
Glutamic	90	120	150
Oxalic	90	120	150
Malonic	60	60	60
Succinic	60	100	100
Citric	80	120	180
Tartaric	60	100	150
Phthalic	60	60	75
Phenylacetic	60	75	100
Salicylic	60	75	90
Caprilic	100	150	200
Ascorbic	60	80	100

UV photolysis time can be reduced, if desired, by increasing the amount of hydrogen peroxide.

For the determination of cationic impurities, *viz.*, iron(III), lead(II), copper(II), cobalt(II), manganese(II), zinc(II) and nickel(II), complete destruction of all types of carboxylic acids was found to be unnecessary. Carboxylic acids (L) forming weaker complexes with the metal ions (M), than the metal–oxalate (Ox) complex formed by the eluent do not require destruction/decarboxylation of the acid by UV photolysis, as the oxalate ion of the eluent is capable of displacing the weak carboxylate ion from the M–L complex, *i.e.*, M–L + Ox → M–Ox + L, and thereby separating various metal ions, which further complex with 4-(2-pyridylazo)-resorcinol monosodium salt and are detected and quantitated. This has been found to be true in the case of aliphatic monocarboxylic acids of low molecular mass, especially formic, acetic, propanoic and butyric acids. On the other hand, di-, poly- and/or hydroxy-substituted carboxylic acids capable of forming stronger M–L complexes (compared with M–Ox complexes) require matrix destruction prior to ion chromatographic analysis. Detailed investigations were made on "synthetic solution 2" consisting of 1000 ppm each of malonic, oxalic, tartaric, citric, salicylic and phthalic acids. A 1-ml volume of this solution was spiked with 50 μg/l each of Fe(III), Cu(II), Pb(II), Mn(II), Co(II), Zn(II), and Ni(II), treated with 1 ml of H_2O_2 and subjected to UV photolysis at 85 ± 5°C. A 20-μl aliquot of HNO_3

(5 *M*) was added after 30 min to ensure the dissolution of the oxides or other insoluble metallic species formed during the course of sample pretreatment and the samples were analysed after different periods of photolysis. The recovery of Fe(III), Pb(II), Cu(II) and Zn(II) was quantitative within 1 h of photolysis, while Co(II) and Ni(II) require at least $1\frac{1}{2}$ h for their complete recovery. The recovery of Mn(II) could not be ascertained, as it is probably oxidized to a higher oxidation state. These findings are summarized in Table II.

In all subsequent studies, carboxylic acids were subjected to 2 h of UV photolysis, to ensure the complete recovery of all the cationic impurities under investigation.

Effect of UV photolysis on impurity ions

The effect of hydrogen peroxide and UV radiation on various anions and cations was investigated in detail. "Synthetic solutions 1 and 2" were spiked with 1 mg/l of many common anions and cations, respectively, and subjected to UV photolysis for 4 h, followed by ion chromatographic analysis.

It was found that the recovery of chloride, bromide, phosphate, sulphate, iron(III), lead(II), copper(II), zinc(II), nickel(II) and cobalt(II) ranged between 97% and 102%, while iodide, nitrite, nitrate and sulphite were lost owing to the influence of UV radiation. It was also found that manganese(II) was oxidized to a higher oxidation state. Hence the present meth-

TABLE II

RECOVERY OF VARIOUS METAL IONS AFTER DIFFERENT UV PHOTOLYSIS TIMES

Metal ion	Recovery (%) after					
	30 min	45 min	60 min	75 min	90 min	120 min
Pb(II)	78	92	102	101	102	100
Cu(II)	84	95	102	100	101	101
Mn(II)	44	58	69	62	56	51
Co(II)	51	61	72	89	101	101
Zn(II)	67	83	101	100	102	101
Ni(II)	37	48	63	77	102	98
Fe(III)	39	86	102	101	102	102

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od of sample pretreatment is not recommended for the determination of manganese(II) and the above-mentioned anions, if present, in carboxylic acids.

EXPERIMENTAL

Reagents and standards

Sodium carbonate, sodium hydrogencarbonate, oxalic acid, lithium hydroxide, 4-(2-pyridylazo)-resorcinol monosodium salt (PAR) and pyridine-2,6-dicarboxylic acid (PDCA) were chromatographic grade (Novachimica, Milan, Italy), hydrogen peroxide (30% m/m, without stabilizer), ammonium hydroxide (30%), sodium hydroxide, glacial acetic acid and nitric acid (70%) were Elbatron electronic grade (Carlo Erba Reagenti, Milan, Italy), and sulphuric acid was analytical grade (Carlo Erba Reagenti). Ammonium acetate (2 M, pH 5.5) was chelation grade (Dionex, Sunnyvale, CA, USA). Ultrapure water with conductivity <0.1 μS (DI water) was obtained from a Milli-Q (Millipore, Bedford, MA, USA) four-bowl deionization system.

Working standards were prepared daily by diluting Carlo Erba Reagenti Normex atomic absorption standards (1.000 g/l) or by dissolving the required Carlo Erba Reagenti analytical-grade reagents.

Quartz test tubes and all glassware were cleaned in concentrated nitric acid and carefully washed with DI water. Normal precautions for trace analysis were observed throughout.

Eluent, regenerant and post-column reagent solutions

A 2.0 mM sodium carbonate–0.75 mM sodium hydrogencarbonate solution was used as chromatographic eluent for anions.

A 2.5 mM sulphuric acid solution was used as regenerant for the anion micromembrane suppressor at 8 ml/min flow-rate.

For the analysis of lead(II), copper(II), manganese(II), cobalt(II), zinc(II) and nickel(II), a mixture of 50 mM oxalic acid and 95 mM lithium hydroxide (pH 4.8) was used as the eluent. While a mixture of 6 mM PDCA, 90 mM acetic acid and 40 mM sodium hydroxide (pH 4.6) was

employed for the determination of iron(III). 0.2 mM PAR dissolved in 3 M ammonium hydroxide and 1 M acetic acid was used as the post-column reagent for cationic analysis with both the eluents.

Instrumentation

Carboxylic acid samples were subjected to UV photolysis in a Metrohm (Herisau, Switzerland) 705 UV digestor equipped with a 500-W high-pressure mercury lamp. The temperature of the sample was maintained at 85 ± 5°C with the help of a combined air/water cooling system.

Chromatographic analysis were performed on a Dionex (Sunnyvale, CA, USA) 2000i ion chromatograph equipped with an EDM eluent degassing module, a GPM gradient pump, an IonPac AG9 guard column and an IonPac AS9 separator column (for anions), an AMMS anion micromembrane suppressor, an IonPac CG5 guard column and an IonPac CS5 separator column (for cations), an IonPac MRAD membrane reactor coupled with a reagent delivery module for post-column reagent addition and a CDM conductivity detector and a VDM2 UV-visible absorbance detector.

Injections of 25 μl of sample were performed.

All measurements were made at 25 ± 1°C, and in all cases injection of the sample was done at least in triplicate.

Precautions were taken to ensure that the analyte did not remain either on the column or on the injection loop overnight. At the end of the analysis, the membrane reactor device was washed with 0.1 M ammonium hydroxide. The injection loop was washed with DI water prior to each analysis.

Peak areas were obtained using AI-450 Dionex software, and background correction was applied wherever necessary.

During the determination of anions, the eluent flow-rate was maintained at 1.5 ml/min, while for cations the eluent flow-rate was 1.0 ml/min and that of the post-column reagent was 0.5 ml/min; the total flow-rate (1.5 ml/min) was checked at the exit of the waste line. For optimal signal-to-noise ratio, the output was measured at a wavelength of 520 nm.

Sample preparation

A amount of 50–100 mg of carboxylic acid was weighed into a quartz tube and 2 ml of hydrogen peroxide were added. The quartz tube was closed with its proper conical PTFE stopper, which tapered to a point. The stopper acted as a cooling finger, prevented solution losses and also protected samples against contamination. The sample was subjected to UV photolysis at 85 ± 5°C for 120 min. The volume was made up to 5 ml and analysed by ion chromatography for determining anionic impurities. For the determination of cationic impurities, 10 μl of 2 M nitric acid were added to ensure the dissolution of all the metallic oxides, if formed during the course of UV photolysis, followed by the addition of 200 μl of 2 M ammonium acetate to maintain the sample pH in the range 5–6, prior to chromatographic analysis. The volume was made up to 5 ml with DI water.

RESULTS AND DISCUSSION

The detection limits of various anions and cations were determined by spiking "synthetic solutions 1 and 2" with varying amounts of different anions and cations, and subjecting them to UV photolysis for 2 h, followed by ion chromatographic analysis. The linearity range

and limits of detection for the anions and cations determined are summarized in Table III.

As evident from Table III, the present method is highly suitable for the determination of very low amounts of iron(III), lead(II), copper(II), zinc(II), nickel(II) and cobalt(II), but suffers from the drawback that cadmium(II) and manganese(II) coelute. Further, the retention times of lead(II) (2.8 min) and copper(II) (3.4 min) are very close to each other; hence, only if these two ions are present in amounts less than 2 μg/ml each, the peaks are well separated.

Sodium, potassium, ammonium, calcium and magnesium at levels higher than 1:1000 do not interfere in the determination of iron(III), lead(II), copper(II), zinc(II), nickel(II) and cobalt(II).

Since many carboxylate ions elute very close to the common inorganic anions, *viz.*, chloride, phosphate and sulphate, interferences due to the simultaneous presence of common inorganic and carboxylate anions were investigated in detail.

It was found that citrate interferes in the determination of chloride, succinate interferes in the determination of phosphate and malonate interferes with the determination of sulphate, if present in amounts greater than those reported in Table IV. Interestingly, the above-mentioned

TABLE III

DETECTION LIMITS AND LINEARITY RANGE FOR VARIOUS IONS DETERMINED IN CARBOXYLIC ACIDS AFTER SAMPLE PRETREATMENT

Ion	Detection limit (μg/l)	Range of linearity (μg/l)
Cl⁻	10	20–2000
Br⁻	20	40–2000
PO₄³⁻	25	50–1500
SO₄²⁻	25	50–2000
Cu(II)	5	50–2000
Pb(II)	10	20–1000
Zn(II)	10	25–1500
Fe(III)	5	15–2000
Ni(II)	25	50–2000
Co(II)	10	20–2000

TABLE IV

TOLERANCE LIMITS (IN mg/l) OF THE VARIOUS CARBOXYLATE IONS DURING THE DETERMINATION OF 1 mg/l OF EACH OF CHLORIDE, PHOSPHATE AND SULPHATE

Carboxylate ion	Chloride	Phosphate	Sulphate
Formate	5	50	1000
Acetate	5	50	1000
Citrate	0.5	30	1000
Benzoate	5	20	800
Succinate	–	5	10
Malonate	–	100	15
Salicylate	–	800	200
Oxalate	–	800	200
Phthalate	–	400	100
Tartrate	20	50	500
Ascorbate	5	150	500
Lactate	5	150	500

interferences during the determination of anions were overcome by the sample pretreatment involving UV photolysis.

The present sample pretreatment method coupled with ion chromatography was applied to determine the impurities in different commercial carboxylic acids. Most of the carboxylic acids were found to contain chloride, sulphate and phosphate as the anionic impurities, while common cationic impurities were found to be iron(III), lead(II), copper(II) and zinc(II).

CONCLUSIONS

UV photolysis of the carboxylic acids followed by ion chromatography was found to be very effective for the simultaneous determination of many inorganic anionic as well as cationic impurities in carboxylic acids. The various ions can be very well determined in the range between 0.6 μM and 1 μM as the present method has excellent resolution, sufficient precision and is more convenient than traditional methods.

REFERENCES

1 Prolabo, *Normes Analytiques des Réactifs*, Rhone-Poulenc, Paris, 1980.
2 J.G. Tarter, *Ion Chromatography*, Marcel Dekker, New York, 1987.
3 H. Small, *Ion Chromatography*, Plenum Press, New York, 1989.