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Journal of Chromatography A, 1067 (2005) 191–196

JOURNAL OF CHROMATOGRAPHY A

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Short communication

# Ion chromatography–electrospray mass spectrometry for the identification of low-molecular-weight organic acids during the 2,4-dichlorophenol degradation

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## Abstract

End-product identification of organic pollutants during oxidation water treatments is of environmental concern due to their potential toxicity. In this work the coupling of ion chromatography (IC), equipped with a membrane ion suppressor, and electrospray ionization mass spectrometry (ESI-MS) has been successfully exploited for the identification of novel low molecular weight organic acids formed as final by-products of 2,4-dichloro-phenol (DCP) degradation by Fenton's reagent, an oxidation method widely employed to degrade recalcitrant organic pollutants in industrial wastewater. The IC–ESI-MS analytical set-up not only allowed the detection of known organic acids but also the identification of 13 new low molecular weight organic acids as a result of extensive oxidation of the parent organic pollutant. Some of the novel organic acids were shown to be chlorine containing by-products and, consequently, of environmental concern. The analytical set-up could be used for characterizing the unknown organic carbon fraction arising from oxidation water treatments.

*Keywords:* Water analysis; Ion chromatography; Mass spectrometry; Organic acids; Oxidation by-products

## 1. Introduction

Identification of by-products arising from organic pollutant degradation in water treatments, such as biological oxidation [1], disinfection [2] and chemical oxidation [3] is a key step in assessing the environmental fate of such pollutants. In fact, identifying by-products, whose toxicity may be even higher than that of the parent compounds [4], is an important issue as little is known about their nature. The identification of such by-products, usually carried out by GC/MS and LC/MS, is not exhaustive, as a large fraction of the total organic carbon present in the solutions analyzed still remains unknown [2]. This is because the by-products are further degraded to organic acids not LC detectable in standard reverse phase operation mode. Accordingly, in order to identify these latter end by-products, ion chromatography (IC) or ion exclusion chromatography (IEC) with conductivity detection, i.e. without MS, have been employed making the detection of some organic acids possible on the basis of the authentic standards available [5]. However, IC–MS and IEC–MS have not been employed up to now for the identification of novel ionic by-products arising from organic pollutant degradation even though these techniques have been successfully used for the detection of organic as well as inorganic species [6–12] in a number of applications where low detection limits were also required [13–16]. In particular, in IC–ESI-MS the use of a membrane ion suppressor has been proved to remove effectively from the mobile phase the sodium ions that cause the formation in the MS interface of uncharged species (i.e. organic/inorganic anion and sodium ion as counter-ion). The latter decreases the transfer efficiency from the atmospheric part of the interface to the vacuum region causing, in turn, a decrease of MS detection sensitivity. Therefore, the use of an ion suppressor makes it possible to combine the advantages of the unique selectivity offered by IC with the specificity and structural elucidation capability of MS [6,14, 16,17].

In the present work the coupling of IC, equipped with a membrane ion suppressor, and ESI-MS has been successfully

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doi:10.1016/j.chroma.2004.12.058

used to identify low molecular weight organic acids during the degradation of 2,4-dichloro-phenol (DCP) by Fenton's reagent ($Fe^{2+}/H_2O_2$), a typical chemical oxidation method widely used to degrade recalcitrant organic pollutants in industrial wastewater [19]. 2,4-Dichloro-phenol has been selected as a model organochloro pollutant as it has been frequently found in industrial landfill leacheates.

## 2. Experimental

### 2.1. Chemicals and Fenton's reactions

2,4-Dichloro-phenol of purity higher than 98% (Aldrich) was used as-received. Hydrogen peroxide solution (ca. 300 g/L) was from Baker and its concentration was assayed iodometrically before each experiment. Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, 99.5%), sulfuric acid and potassium hydroxide were obtained from Carlo Erba (Italy) and were used as-received. Water used for IC as well as for preparing all aqueous solutions (18.2 MΩcm, organic carbon content $\leq 4\ \mu g/L$) was obtained by a Milli-Q Gradient A-10 system (Millipore). NaOH for IC was from Baker. Reagent stock solutions were prepared daily.

Details about Fenton's reactions are reported elsewhere [20]. Initial reagent concentrations (total volume 500 mL) were as follows: [DCP] = 2.3 mM, $[Fe^{2+}]$ = 0.1 mM and $[Cu^{2+}]$ = 0.1 mM. The progress of the reactions was monitored at scheduled reaction times by withdrawing 2 mL samples that were immediately frozen.

### 2.2. Ion chromatography–mass spectrometry

Organic acids as well as inorganic anions determination were carried out by a GS50 system (Dionex) equipped with an AS50 autosampler, an ED50 conductivity detector and a ASRS-ultra suppressor, operated at 100 mA in external water mode. Samples, injected via a 25 μL loop, were eluted at a flow rate of 0.5 mL/min through an analytical IonPac AS-11 column (250 mm × 2 mm) equipped with a IonPac AG-11 guard-column (50 mm × 2 mm) with the following gradient: from 10/0/90 (NaOH 5 mM/NaOH 100 mM/water), held for 2.5 min, to 100/0/0 in 3.5 min, then to 50/50/0 in 12 min, held for 5 min.

The flow from the conductivity detector of the IC system was split 1:1, by means of a zero dead volume T-piece, to allow one half to enter a Ultimate series UV detector (LC-Packing Dionex), set at 220 nm, and the other half to enter the mass spectrometer interface. The optimization of the ESI-MS interface was performed by using just the ionPac AG-11 guard column in isocratic mode (0/20/80 of NaOH 5 mM/NaOH 100 mM/water) at a flow rate of 0.5 mL/min. These analytical conditions were carefully chosen in order to elute all the organic acids within 2 min and, consequently, to run several injections during a MS acquisition for optimizing each ESI interface parameter. Ten microliters of a standard solution of organic acids (1 mg/L) was injected through a 7125-Ti Rheodyne valve.

An API 165 mass spectrometer (Applied Biosystems/MSD Sciex) equipped with a turboionspray interface was used throughout the present work. The resolution of the mass spectrometer was set so that peaks full width at half-height was 0.7 Da. Full scan acquisition were acquired in negative ion mode using 0.1 amu step sizes with a dwell time of 0.8 ms, resulting in total scan time of 2.16 s. Other mass spectrometric conditions were as follows: nebulizer gas flow (air) = 1.5 L/min, curtain gas flow (nitrogen) = 1 L/min, mass range = 30–300, needle voltage = −4000 V, orifice voltage = −25 V, ring voltage = −110 V, auxiliary gas flow (air) delivered by a turbo heated probe = 6 L/min at 450 °C.

## 3. Results and discussion

An optimization of the ESI-MS interface was initially performed in order to verify whether standard HPLC–MS parameters apply to organic acids detection. It was found that a careful optimization of the critical ESI-MS parameters (needle voltage, orifice voltage, ring voltage and auxiliary gas temperature), carried out with citric, muconic and chloracetic acids as representative compounds, allowed an increase of $[M-H]^-$ intensities of more than one order of magnitude with respect to standard HPLC–MS parameters. In particular, the parameter that most affected the sensitivity was the ring voltage showing a gain between two- and four-fold (Fig. 1) with respect to the standard value (−200 V). In addition, the influence of methanol was also investigated as it has been reported that adding it can result in an increase in MS sensitivity [14,21]. However, it was found that methanol addition did not cause any improvement of the sensitivity of the $[M-H]^-$ ions probably because in the interface used the

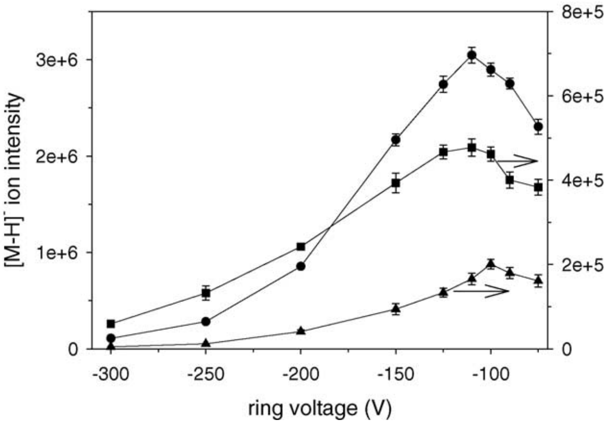

Fig. 1. Dependence of the intensity of $[M-H]^-$ ions (citric acid (●), muconic acid (■) and chloroacetic acid (▲)) on ring potential. Plotted data points are averages of duplicate measurements. Other MS conditions: nebulizer gas flow (air) = 1.5 L/min, curtain gas flow (nitrogen) = 1 L/min, mass range = 30–300, needle voltage = −4000 V, orifice voltage = −25 V, auxiliary gas flow (air) delivered by a turbo heated probe (450 °C) = 6 L/min.