

## Short communication

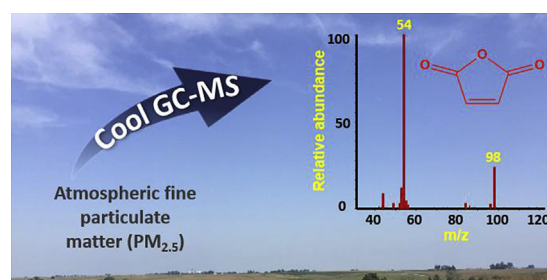
## Quantification of furandiones in ambient aerosol



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## GRAPHICAL ABSTRACT



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## ABSTRACT

Furandiones are products of the photooxidation of anthropogenic volatile organic compounds (VOC), like toluene, and contribute to secondary organic aerosol (SOA). Because few molecular tracers of anthropogenic SOA are used to assess this source in ambient aerosol, developing a quantification method for furandiones holds a great importance. In this study, we developed a direct and highly sensitive gas chromatography-mass spectrometry method for the quantitative analysis of furandiones in fine particulate matter that is mainly free from interference by structurally-related dicarboxylic acids. Our application of this method in Iowa City, IA provides the first ambient measurements of four furandiones: 2,5-furandione, 3-methyl-2,5-furandione, dihydro-2,5-furandione, and dihydro-3-methyl-2,5-furandione. Furandiones were detected in all collected samples with a daily average concentration of  $9.1 \pm 3.8 \text{ ng m}^{-3}$ . The developed method allows for the accurate measurement of the furandiones concentrations in ambient aerosol, which will support future evaluation of these compounds as tracers for anthropogenic SOA and assessment of their potential health impacts.

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## 1. Introduction

Atmospheric particulate matter (PM) significantly affects human health (Dockery et al., 1993) and the Earth's climate (IPCC, 2007). Primary sources emit PM directly to the atmosphere, while secondary aerosol forms in the atmosphere. Secondary organic

aerosol (SOA) forms by chemical reactions of volatile organic compounds (VOC) followed by condensation to the particle-phase. These reactions depend, in part, on the presence of available precursors and oxidants and the chemistry of existing particles (Kroll and Seinfeld, 2008). Current knowledge of the precursors, mechanisms of formation, and properties of SOA is incomplete, leaving major gaps in understanding of exactly how, and to what extent, SOA affects air quality and climate (Foley et al., 2010).

The relative roles of natural and anthropogenic precursors to

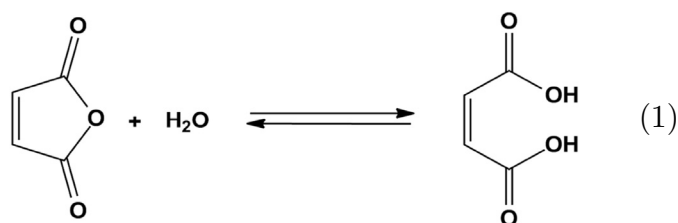
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SOA remain highly uncertain. Some studies indicate dominance (>90%) of biogenic precursors like isoprene (Hallquist et al., 2009), while others studies highlight the importance of anthropogenic VOC (>30%), such as benzene and toluene (Henze et al., 2008; Volkamer et al., 2006). SOA products from aromatic VOC can help to constrain estimates of anthropogenic SOA contributions to ambient PM through an SOA tracer approach (Kleindienst et al., 2007). To date, anthropogenic SOA tracers are limited to one toluene oxidation product (2,3-dihydroxy-4-oxopentanoic acid) (Kleindienst et al., 2004; Offenberg et al., 2007) that has been used quantitatively and poly-carboxylic acids that have been used qualitatively (Fine et al., 2004). Other classes of compounds, such as furandiones, nitrophenols, and nitrobenzenes are products of benzene, toluene, xylenes, and other alkyl benzene SOA (Forstner et al., 1997; Hamilton et al., 2003; Kleindienst et al., 1999; Koehler et al., 2004; Volkamer et al., 2006) and may prove to be useful tracers.

Furandiones, in particular, are among the most frequently identified products of aromatic VOC oxidation in the presence of nitrogen oxides (NO<sub>x</sub>) (Bandow et al., 1985). They form through a ring opening mechanism, by which toluene or an alkyl benzene ring reacts with an OH radical in the presence of NO<sub>x</sub>. This process leads to the cleavage of the benzene ring to form a *cis*-butendial intermediate which undergoes cyclization leading to the formation of 2,5-furandione (Bandow et al., 1985; Forstner et al., 1997; Jang and Kamens, 2001). Forstner et al. (1997) have reported that 3-methyl-2,5-furandione, 2,5-furandione, and dihydro-2,5-furandione represent 58% of the total identified mass resulting from toluene, 66% from *m*-xylene, 35% from ethylbenzene, 34% from 1,2,3-trimethylbenzene, and 31% from *m*-ethyltoluene photooxidation in the presence of NO<sub>x</sub>.

The potential for human exposures to furandiones in ambient air is significant, due to their adverse effects on the respiratory system. For example, acute inhalation of 2,5-furandione has been the source of irritation of the respiratory tract and chronic exposure has caused bronchitis, bronchial asthma, and irritation of the nose and eyes (CDC, 2015; EPA, 1992). 2,5-Furandione and dihydro-2,5-furandione, in particular, have been shown to produce these effects in human as well as in animal tests (EPA, 1992; NIH). Although less data is available on dihydro-2,5-furandione, there is evidence that it irritates the eyes, skin, and respiratory tract (NIH). Assessing the potential health effects of outdoor exposures to furandiones requires knowledge of their ambient concentrations.

The water-sensitivity of these compounds presents analytical challenges in their measurement. Furandiones are anhydrides that undergo a ring opening reaction in the presence of water. Shown in Eq. (1) is 2,5-furandione reacting with water to form (2Z)-2-butenedioic acid. Consequently, water must be avoided in sample preparation and analysis.



In general, dicarboxylic acids can lose a water molecule and form the corresponding anhydride at temperatures > 150 °C (i.e. the reverse reaction shown in Eq. (1)). The specific temperature at which this reaction occurs varies by species (Koehler et al., 2004). Because dicarboxylic acids are ubiquitous in the atmosphere, there is potential for anhydrides to form as artifacts of analysis by gas

chromatography, where high temperatures are encountered (Dilorenz, 1971).

Although numerous chromatographic methods have been developed for quantification of furandiones, their ambient concentrations have yet to be quantified. Predominantly, a derivatization step has been used to reduce the reactivity of these compounds and improve the chromatographic accuracy and reproducibility (CDC, 2015; Dahlin et al., 2004; Geyer and Saunders, 1986). However, with derivatization, it becomes impossible to distinguish between anhydrides and their corresponding dicarboxylic acids that are often present in the sample matrix; consequently, reported values are the sum of acids and anhydrides. Only a few methods have discussed the direct quantification of furandiones without derivatization. Direct gas chromatography-mass spectrometry (GC-MS) methods were used to quantify furandiones in smog chambers (Forstner et al., 1997; Hamilton et al., 2005) and indoor occupational settings (Pfaffli et al., 2002). All of these methods involve using a temperature  $\geq 230$  °C during sample preparation and/or analysis. At such a high temperature, the dicarboxylic acids in the sample matrix undergo interconversion to their anhydride, introducing quantification artifacts.

In the present study, a reduced temperature gas chromatography-mass spectrometry (GC-MS) method was developed, validated, and applied to the direct quantification of furandiones in atmospheric aerosol. Target analytes included 2,5-furandione (FD), 3-methyl-2,5-furandione (MFD), dihydro-2,5-furandione (DFD), and dihydro-3-methyl-2,5-furandione (DMFD). Method validation included assessing positive and negative analysis artifacts on quantification. Also, the current study introduces an efficient protocol for extraction and recovery of furandiones from quartz fiber filters. Our results include the first measurements of furandiones in ambient fine particulate matter (PM<sub>2.5</sub>).

## 2. Materials and methods

### 2.1. Sample collection

PM<sub>2.5</sub> filter samples were collected daily from September 26 to October 6, 2014 in Iowa City, IA, USA (+41.6572, -91.5035). PM<sub>2.5</sub> was collected with a medium-volume URG air sampler (3000B, URG Corp.) with a cyclone (URG) operating at a flow rate of 90 L min<sup>-1</sup>. The sampler was installed on a wooden platform, and the inlet was positioned 3.5 m above ground level. Samples were collected on 90-mm quartz fiber filters (Pallflex<sup>®</sup> Tissuquartz<sup>™</sup>, Pall life science) that were pre-cleaned by baking for 18 h at 550 °C. Air flow rate was monitored before and after sampling using a rotameter (Gilmont Inst.). Samples were collected for 23 h, and filter changing was performed at 8:00 a.m. (CST). After sample collection, filters were transferred to Petri dishes, enveloped with prebaked aluminum foil, sealed with Teflon tape, and stored frozen at -20 °C until analysis. One field blank was collected for every five samples. Hourly PM<sub>2.5</sub> mass measurements were obtained from the Iowa Department of Natural Resources (DNR) nearby air quality monitoring site (+41.6572, -91.5035) located 3.2 km east of the filter sampling site (EPA, Accessed November 20, 2015). PM<sub>2.5</sub> mass data were only used for filter sampling periods when hourly measurements were available for the entire sampling period.

### 2.2. Extraction

Prior to extraction, isotopically labeled internal standards (2,5-furandione-D<sub>2</sub> (Aldrich) and dihydro-2,5-furandione-2,2,3,3-D<sub>4</sub> (Aldrich)) were spiked onto the filter. Filters were extracted sequentially by ultra-sonication with three 10 mL portions of acetonitrile (Optima-Fisher Scientific-Fisher Chemical). The

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