



Comparison of sampling methods for radiocarbon dating of carbonyls in air samples via accelerator mass spectrometry



Matthias Schindler*, Wolfgang Kretschmer, Andreas Scharf, Alexander Tschekalinskij

Physikalisches Institut, Universität Erlangen-Nürnberg, Erwin-Rommel-Str. 1, 91058 Erlangen, Germany

ARTICLE INFO

Article history:

Received 23 December 2015

Received in revised form 18 March 2016

Accepted 19 March 2016

Available online 2 April 2016

Keywords:

AMS

Radiocarbon

Carbonyl

pmC

ABSTRACT

Three new methods to sample and prepare various carbonyl compounds for radiocarbon measurements were developed and tested. Two of these procedures utilized the Strecker synthetic method to form amino acids from carbonyl compounds with either sodium cyanide or trimethylsilyl cyanide. The third procedure used semicarbazide to form crystalline carbazones with the carbonyl compounds. The resulting amino acids and semicarbazones were then separated and purified using thin layer chromatography. The separated compounds were then combusted to CO₂ and reduced to graphite to determine ¹⁴C content by accelerator mass spectrometry (AMS). All of these methods were also compared with the standard carbonyl compound sampling method wherein a compound is derivatized with 2,4-dinitrophenylhydrazine and then separated by high-performance liquid chromatography (HPLC).

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1. Introduction

In recent years, efforts to eliminate the sources of carbonyl-containing compounds such as aldehydes and ketones have resulted in numerous analyses of indoor and outdoor air samples to identify the origins and compositions of these compounds [22,15,23,8]. These pollutants may potentially be present at concentrations above the recommended guidelines in indoor air and are thus hazardous in terms of their allergenic or carcinogenic impacts on humans [27,5,9]. Carbonyl-containing pollutants are often released by man-made products (paints, glues) that contain organic compounds. These anthropogenic substances are normally derived from petroleum, coal, or natural gas. However, carbonyl compounds can also be naturally released in the air via plant emissions or the combustion of natural materials [12]. The carbonyl compounds that are present in outdoor air have been analyzed since it is suspected that their volatile organic compounds (VOCs) are the precursors of ozone. Hence, reduction of VOCs in the troposphere may result in decreased ozone production. Carbonyl-containing compounds can also be generated by the Harries ozonide reaction, wherein organic compounds with multiple carbon-carbon bonds react with ozone [17,10,7,3]. The generation of these carbonyl compounds can be either biogenic or anthropogenic in all of these cases. It is assumed that biogenic carbonyl compounds were recently generated as these compounds possess

a modern ¹⁴C/¹²C ratio that is similar to the detected CO₂ ratio in the environmental atmosphere. Anthropogenic carbonyl compounds are derived from petroleum, which is a type of fossil fuel that does not contain ¹⁴C. The use of biofuels and biosolvents may perturb the information about anthropogenic contribution and is neglected in this simplified model. Therefore, compound specific radiocarbon analysis (CSRA) can be utilized to distinguish the origins of carbonyl-containing compounds in ambient air samples [18].

The majority of targeted carbonyl compounds are gaseous at room temperature. They also may occur in low concentrations of <100 µg/m³ in air samples, which means that these compounds must be derivatized into either their liquid or solid phase to effectively collect and separate the gaseous components. The standard method for measuring the amounts of concentrated aldehydes and ketones involves the reaction of these compounds with 2,4-dinitrophenylhydrazine (DNPH). The reaction of a carbonyl compound with 2,4-DNPH begins with a nucleophilic attack of the amino group at the polarized carbon atom of the carbonyl group (Fig. 1). This process is also considered to be a condensation reaction. This procedure creates hydrazones (with six additional carbon atoms per molecule) that can be effectively separated using HPLC. If the solid or liquid samples contain at least 100 µg of carbon, then the separated hydrazones can be graphitized through combustion with an elemental analyzer to obtain solid targets for radiocarbon measurements. For samples with less than 100 µg carbon the ¹²C- and ¹³C-ion currents and ¹⁴C count rates are too small for meaningful measurement. This method was used by Kato et al. [16] to characterize acetaldehyde from indoor air samples by AMS.

* Corresponding author.

E-mail address: matthias.schindler@physik.uni-erlangen.de (M. Schindler).

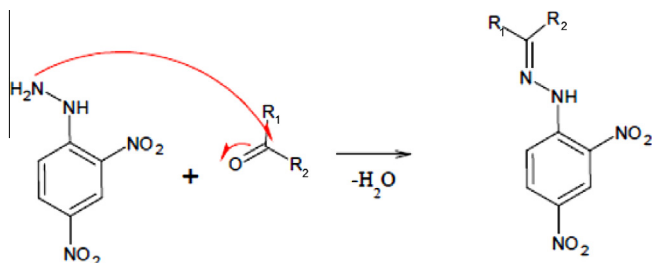


Fig. 1. Formation of 2,4-DNPH.

In the DNPH method, the introduction of six additional carbon atoms during the derivatization process significantly increases the ^{14}C measurement uncertainty of the targeted compounds. We thus chose to devise alternative testing strategies that would introduce a minimal number of carbon atoms during formation of the solid carbonyl derivatives. The first two procedures are based on Strecker type synthesis, wherein an amino acid can be formed from a carbonyl compound by introducing only one additional carbon atom. The first procedure employs the classical Strecker synthesis and uses alkali cyanide as a nitrogen source. The second procedure modifies the Strecker method by employing trimethylsilyl cyanide (TMSCN) as a cyanide source to increase the reaction efficiency. The third procedure involves the formation of semicarbazones with the introduction of only one extraneous carbon atom. This latter method can only be applied to aldehydes that have more than one carbon atom, which means that this method is not suitable for the analysis of formaldehyde, because it is known that semicarbazide and formaldehyde do not react directly to yield a normal semicarbazone [11]. All of the samples used to perform these newly developed methods were purified using thin layer chromatography (TLC).

2. Methods

2.1. Chemical reactions

2.1.1. Classical Strecker synthesis

In the first step (Fig. 2), the aldehyde/ketone reacts with ammonia to form an imine (nitrogen double bond). This step occurs very quickly and provides an excellent yield of the corresponding intermediate.

The imine is then reacted with cyanide ions from hydrolysis of sodium cyanide to form an aminonitrile (Fig. 3). The resulting aminonitrile is treated with an acidic solution to form a D,L-amino acid salt. The amino acid is released from the salt by alkalinizing the dissolved salt to a pH of 8 using tri-*n*-butylamine (Fig. 4).

2.1.2. Modified Strecker synthesis with TMSCN

The first step of the modified Strecker synthesis involves the formation of an O-silylated cyanohydrin from the carbonyl compound and TMSCN (Fig. 5). In the next step, a nucleophilic attack of the amine transforms the cyanohydrin into an aminonitrile.

The aminonitrile is then hydrolyzed under acidic conditions to form its corresponding D,L-amino acid salt. The salt is then diluted



Fig. 2. Aldehyde ($R_2 = \text{H}$) or ketone ($R_2 = \text{C}$) react to form imines.

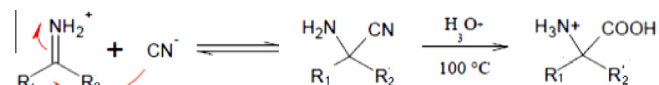


Fig. 3. Imine reacts with cyanide to form aminonitrile that is subsequently hydrolyzed by acetic acid to form amino acid salt.

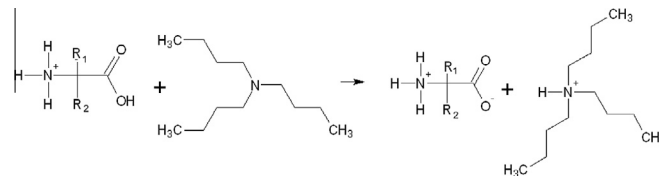


Fig. 4. Liberation of amino acids by tri-*n*-butylamine.

with water and treated with an excess of tri-*n*-butylamine to release the amino acid.

2.1.3. Formation of semicarbazones

Semicarbazones are formed by the reaction of an aldehyde/ketone with a semicarbazide under slightly acidic conditions. This process is considered to be a condensation reaction since a molecule of water is released through the combination of the two aforementioned molecules (Fig. 6).

2.2. Experimental

The chemicals and reagents used in the experiment are listed in Table 1.

2.2.1. Spiking of air samples

Spiking the air with carbonyls was performed by introducing a solution, containing the target carbonyl, to a washing bottle. The carbonyl solution was prepared by dissolving and diluting the carbonyl in water. If the carbonyl was insoluble in water, methanol was added. To get gaseous samples air was constantly pumped through the washing bottle. In order to ensure that all carbonyl was vaporized, the washing bottle was heated up to 45 °C. The spiked air was then used to test the derivatization and sampling methods.

2.2.2. Classical Strecker syntheses [25,26]

A gas-washing bottle, filled with a mixture of 2 g of ammonium chloride, 20 ml of a concentrated ammonia solution, 30 ml of water, 10 ml of methanol, and 2.5 g of sodium cyanide, was used to sample a large amount of air. A mobile air-sampling pump (model SD 820, VWR, Germany) bubbled the air through the mixture at a flow rate of 7 L/min for at least 48 h. The reaction efficiency was increased by using fritted glass to obtain very small bubbles, which maximized the reaction rate in the first step (imine formation). A second bottle containing a caustic soda solution (20 %) to trap hydrogen cyanide was coupled to the outlet of the gas-washing bottle. After the air sampling had been completed, the mixture in the first washing bottle was evaporated at a temperature between 30 °C and 40 °C with a vacuum until approximately 10 ml of the solution remained. Then, 20 ml of concentrated hydrochloric acid was added, and the solution was refluxed for 4 h to hydrolyze the aminonitrile. The mixture was then vacuum-dried, and the resultant residue was dissolved in 10 ml methanol and filtered. The filtrate was alkalinized to a pH of 8 with tributylamine to release the amino acids. The amino acids were then fully crystallized in the refrigerator, and the resulting crystals

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