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RESEARCH PAPER

A new sensitive method for the quantification of glyoxal and methylglyoxal in snow and ice by stir bar sorptive extraction and liquid desorption-HPLC-ESI-MS

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Abstract In this study, the development of a new sensitive method for the analysis of alpha-dicarbonyls glyoxal (G) and methylglyoxal (MG) in environmental ice and snow is presented. Stir bar sorptive extraction with in situ derivatization and liquid desorption (SBSE-LD) was used for sample extraction, enrichment, and derivatization. Measurements were carried out using high-performance liquid chromatography coupled to electrospray ionization tandem mass spectrometry (HPLC-ESI-MS/MS). As part of the method development, SBSE-LD parameters such as extraction time, derivatization reagent, desorption time and solvent, and the effect of NaCl addition on the SBSE efficiency as well as measurement parameters of HPLC-ESI-MS/MS were evaluated. Calibration was performed in the range of 1–60 ng/mL using spiked ultrapure water samples, thus incorporating the complete SBSE and derivatization process. 4-Fluorobenzaldehyde was applied as internal standard. Inter-batch precision was <12 % RSD. Recoveries were determined by means of spiked snow samples and were 78.9±5.6 % for G and 82.7±7.5 % for MG, respectively. Instrumental detection limits of 0.242 and 0.213 ng/mL for G and MG were achieved using the multiple reaction monitoring mode. Relative detection limits referred to a sample volume of 15 mL were 0.016 ng/mL for G and 0.014 ng/mL for MG. The optimized method was applied for the analysis of snow samples from Mount Hohenpeissenberg (close to the Meteorological Observatory Hohenpeissenberg, Germany) and samples from an ice core from Upper Grenzgletscher (Monte Rosa massif, Switzerland). Resulting concentrations were 0.085–16.3 ng/mL for G and 0.126–3.6 ng/mL for MG. Concentrations of G and MG in snow were 1–2 orders of magnitude higher than in ice core samples. The described method represents a simple, green, and sensitive analytical approach to measure G and MG in aqueous environmental samples.

Keywords Glyoxal · Methylglyoxal · SBSE · Liquid desorption · HPLC-MS · Ice

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Introduction

The two smallest alpha-dicarbonyls glyoxal (G) and methylglyoxal (MG) have received increasing scientific interest in recent years due to their important role in the formation and growth of secondary organic aerosol (SOA) [1]. SOA itself is of great interest because of its impact on the radiative budget of the earth's atmosphere [2]. G and MG are formed through gas phase oxidation of volatile organic compounds (VOCs) of both anthropogenic (i.e., aromatics, alkenes) and biogenic (i.e., isoprene) origin [1, 3, 4]. Besides secondary formation, G and MG can also be emitted directly into the atmosphere by biomass burning [1]. The lifetime of the alpha-dicarbonyls in the gas phase is rather short (about 2 h) [5]. However, due to their high Henry's law coefficients, G and MG efficiently partition into the (aqueous) particle phase. Besides, the compounds are easily scavenged by precipitation (i.e., fog, cloud droplets, rain, or snow), either directly from the gas phase or as component of aerosol particles [6, 7]. In the

aqueous phase, G and MG reversibly form hydrated monomers and oligomers. Through further aqueous phase chemistry (particularly in cloud water), alpha-dicarbonyls can be oxidized by OH radicals to form organic acids, especially oxalic and pyruvic acid, which are found in SOA [8]. Oligomerization of either G/MG or their oxidation products can also contribute to SOA formation [9, 10].

In high altitude and latitude regions, snow is the only type of precipitation. After scavenging and deposition, organic compounds in the seasonal snow layer may undergo transformation processes such as physical exchange ("wind pumping"), photochemical production from other precursors or degradation [11, 12]. Until now, very little is known about the role of the small, water-soluble compounds G and MG in these complex processes. Their determination is of high interest and can possibly give insight into chemical processes occurring in the ice. By analyzing ice core samples, information about the atmospheric composition in the past - interrelated with the climate - is accessible. In addition to studies focusing on the quantification of organic compounds, like for example VOCs, persistent organic pollutants, or carboxylic acids in snow and ice (e.g., [13–15]) there are only few studies targeting G and MG in snow and frost flowers ([16–18]), as well as in ice cores ([19]).

The analysis of carbonyl compounds usually comprises a derivatization step. This is crucial regarding GC analyses as it improves volatility and stability of the analytes, for example. A commonly used derivatization approach is pentafluorobenzyl hydroxylamine (PFBHA) derivatization with GC-ECD detection [20]. A study using PFBHA derivatization in combination with GC-MS was recently presented for the analysis of G and MG in seawater and marine aerosol [5]. Derivatization with BF_3/n-butanol, which yields the corresponding dibutyl acetals, was applied for the measurement of G and MG in rain and snow, also using GC and GC-MS ([21]). However, with the continuous development of atmospheric pressure ionization techniques such as electrospray ionization (ESI), the number of applications using LC and LC-MS has increased enormously over the last decades. The possibility of using various column materials, eluent compositions, and detection modes makes LC(-MS) a promising tool to meet the increasing needs of analytical measurements. Although not obligatory, derivatization is a powerful strategy to enhance the capabilities of LC (-MS) in various ways, i.e., concerning chromatographic, ionization, and detection properties [22]. The most frequently used derivatizing reagent for the analysis of carbonyl compounds with LC is 2,4-dinitrophenylhydrazine (DNPH) [23, 24]. A selective derivatization of alpha-dicarbonyls was also achieved using aromatic diamino compounds such as 2,3-diaminonaphthalene. The resulting highly fluorescent derivatization products were quantified using fluorescence detection [25]. Dansylacetamidooxyamine derivatization with LC-fluorescence detection was used for the highly sensitive analysis of alpha-dicarbonyls and hydroxyacetaldehyde as well as monoaldehydes [17].

The aim of this study was the development of a new simple LC-MS method for the sensitive quantification of G and MG in snow and ice. Stir bar sorptive extraction (SBSE) with in situ derivatization is applied for extraction and enrichment of the analytes. SBSE is an equilibrium technique which uses stir bars with polydimethylsiloxane (PDMS) coating. The extraction is based on the partitioning of the solutes between the siloxane phase (stir bar) and the aqueous sample. In a second step, the analytes are recovered from the stir bar. This is achieved either by thermal desorption using a thermal desorption device attached to a GC system or by liquid desorption (LD). In the latter case, the analytes are desorbed by a solvent with higher elution strength than the original sample. LD is compatible with LC-MS analysis and does not require additional hardware [26]. Compared to solid phase micro extraction, which is based on the same sorptive extraction principle, SBSE requires less technical equipment and can achieve higher extraction efficiency due to a larger volume of the siloxane phase. No time-consuming evaporation of the aqueous sample is needed, as the stir bar can be added directly to the sample. SBSE-LD is a "green" extraction technique, because it is less solvent intensive than liquid–liquid extraction. In contrast to the frequently used solid phase extraction (SPE), SBSE-LD is less labor- and cost-intensive because the stir bars are easy to handle and can be reused multiple times.

To the authors' best knowledge, this method is the first to combine SBSE with in situ benzylhydroxylamine (BHA) derivatization and HPLC-MS/MS for the analysis of G and MG.

Experimental section

Chemicals and materials

G and MG (40 % (*w*) aqueous solutions) were purchased from Acros Organics (Thermo Fisher Scientific, Geel, Belgium). *O*-benzylhydroxylamine hydrochloride (BHA·HCl, 99 %), *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA·HCl, GC derivatization grade), 4-fluorobenzaldehyde (98 %), sulfuric acid (95–98 %), dichloromethane (HPLC grade), acetonitrile (HPLC gradient grade), and formic acid (LC-MS grade) were purchased from Sigma-Aldrich (Steinheim, Germany). Hydrochloric acid (30 %) was obtained from Merck (Darmstadt, Germany). Sodium hydroxide was purchased from Carl Roth (Karlsruhe, Germany). Sodium chloride (HPLC grade) was purchased from Fisher Chemical (Geel, Belgium). Ultrapure water (18.3 MΩ cm) was obtained using a Milli-Q water system from Millipore (Bedford, USA). PDMS-coated stir bars (Twister®, film thickness 1 mm, length 10 mm) were purchased from Gerstel

(Mülheim, Germany). SPE cartridges (Discovery DSC-18, 1 mL, 100 mg bed volume) were purchased from Supelco (Sigma-Aldrich, Steinheim, Germany).

Purification of the derivatization reagent

BHA·HCl was purified adapting a method described by Matsunaga and Kawamura [16]. Briefly, BHA·HCl was dissolved in ultrapure water. Sodium hydroxide pellets were flushed with methanol and added to the solution. Free benzylhydroxylamine was extracted with dichloromethane and precipitated as BHA·HCl by adding 8 M HCl solution. The precipitate was filtered and dried under reduced pressure.

A stock solution was prepared by diluting 125 mg purified BHA HCl in 20 mL ultrapure water. The stock solution was stored at 4 °C and was stable over several months. Prior to sample preparation, an aliquot of the stock solution was purified using SPE with a C18 stationary phase: The SPE cartridge was conditioned with 2×800 μL acetonitrile and washed with 2×800 μL ultrapure water. Four milliliters of the BHA solution were applied to the cartridge by means of a low pressure to retain possible contaminants. The eluted solution was collected and applied for derivatization.

SBSE procedure

All glass vials (sample flasks, extraction vials, liquid desorption vials, and storage vials) were cleaned by heating at 450 °C for 8 h. Prior to use, the stir bars were put in glass vials filled with 2–3 mL acetonitrile and cleaned in an ultrasonic bath for 30 min before stirring in 3 mL fresh acetonitrile at 1,000 rpm overnight. These cleaning steps were repeated after every analysis to avoid carry over.

For extraction, spiked water samples (for calibration) or environmental samples were filled into 20 mL screw-cap vials with PTFE-septa. One hundred fifty microliters of internal standard solution (4-fluorobenzaldehyde) and 100 μL of derivatization solution (BHA) were added. The pH was adjusted to 3.5 with 0.1 M sulfuric acid. The stir bars were removed from the storage vials using magnetic rods, dried carefully with a lint-free tissue and added to the sample solution. The vials were closed tightly and put on a 15-point magnetic stirring plate for 20 h at 1,000 rpm. After extraction, stir bars were removed from the extraction solution and transferred into 5 mL vials containing 1.5 mL acetonitrile as stripping solvent for liquid desorption. After stirring for 3 h at 500 rpm, the stir bars were removed from the vials. The desorption solution was transferred to an autosampler vial and provided for analysis. Stir bars were cleaned as described above and stored in acetonitrile (ACN) until further use. An overview of the SBSE-LD procedure is shown in Fig. 1. During method development, several important SBSE parameters such as extraction time (2–20 h), liquid desorption time (0.5–20 h) and solvent (methanol, acetonitrile) were optimized.

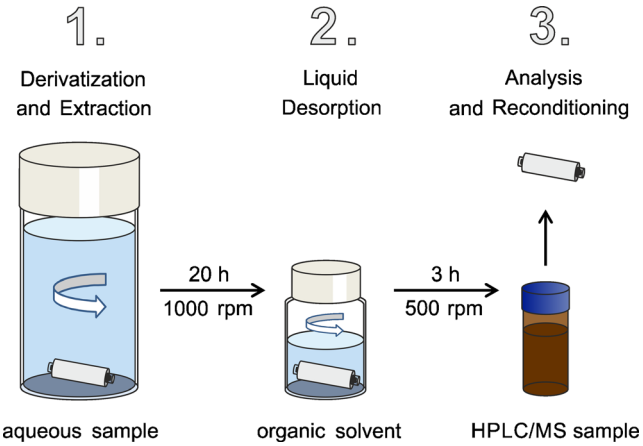

Fig. 1 Sample preparation using SBSE-LD

Liquid chromatography–mass spectrometry

The high-performance liquid chromatography coupled to electrospray ionization tandem mass spectrometry (HPLC-ESI-MS/MS) measurements were carried out using a HPLC system (Agilent 1100 series, composed of degasser, binary gradient pump, auto sampler, column oven, and diode array detector, Agilent Technologies, Germany) coupled to a HCT-Plus ion trap mass spectrometer (Bruker-Daltonics, Bremen, Germany). The analytical column (Pursuit XRs 3 C8 150×2.0 mm, 3 μm particle size, Varian, Germany) was heated to 30 °C during analysis.

Eluent A (ultrapure water with 2 % acetonitrile and 0.04 % formic acid) and B (acetonitrile with 2 % ultrapure water) were used in gradient mode with a constant flow rate of 200 μL/min. The injection volume was 20 μL.

The ESI source was operated in positive ion mode with 35 psi nebulizer pressure, 9 L/min dry gas flow (both N_2), 350 °C dry gas temperature, and 4.5 kV capillary voltage. All other electronic parameters were set using the smart tune option for the respective *m*/*z* values of the analyte molecular ions. Analysis was performed using the multi reaction monitoring (MRM) mode which significantly reduces background noise: The protonated molecular ions $[M + H]^+$ of the derivatization products (*m*/*z* 269 and *m*/*z* 283 for glyoxal-bis-oxime and methylglyoxal-bis-oxime) were isolated and fragmented in the ion trap using collisional induced dissociation (CID). Helium was used as collision gas with optimized fragmentation amplitude of 0.7 (specific parameter of the instrument). The most abundant fragment ions (*m*/*z* 91 for both glyoxal-bis-oxime and methylglyoxal-bis-oxime) were monitored and used for quantification.

Standards

Stock solutions of G and MG with concentrations of 506 and 471 ng/mL, respectively, were prepared daily by diluting the commercially available solutions with ultrapure water. To obtain method development and calibration solutions, volumes of 15 mL ultrapure water were spiked with distinct volumes of G (or MG) stock solution and 5.7 μg/L of the internal standard. The spiked solutions were treated as described in the "SBSE procedure" section above. That way, the calibration standards run through the whole extraction procedure just like the real samples and analyte loss during extraction or liquid desorption is corrected for. Besides, there was no need for synthesizing the bis-oximes (which are not commercially available) as they were formed during the extraction/derivatization process.

For each analyte, five calibration standards were prepared with spiked amounts of G (or MG) ranging from 1 to 60 ng. Blank measurements (n=5) were conducted using 15 mL of ultrapure water to obtain values for the evaluation of the analytical limits and determine contamination levels of glassware, reagents, and stir bars.

Sampling

Snow samples were collected on a field next to the Meteorological Observatory at Hohenpeissenberg on Mount Hohenpeissenberg (977 m a.s.l., 47°48′N, 11°00′E) in Bavaria, Germany. Preheated 500 mL glass sample flasks were filled with snow and sealed firmly using screw caps with PTFE-coated septa. Samples were collected in triplicate from the surface and from 30 cm depth.

Ice core samples were obtained from a 125 m long ice core from the upper Grenzgletscher, Monte Rosa massif (4,200 m a.s.l., 45°55′N, 7°52′E) in the southern Swiss Alps. Drilling and storing conditions as well as glaciochemical dating of the ice core are described elsewhere (see [27, 28]). Samples from two different years (1959 and 1991) were analyzed as a proof of principle.

After collection, all samples were kept frozen and stored at −20 °C. On the day of analysis, the samples were thawed at room temperature and analyzed immediately to prevent any kind of decay.

Results and discussion

Method development

Derivatization

The SBSE efficiency of a particular analyte can be estimated using the octanol/water partitioning coefficient ($K_{O/W}$) which is a reliable approximation for the partitioning coefficient between the PDMS phase and water ($K_{PDMS/W}$). Together with the phase ratio ($V_{\mathrm{Water}}/V_{\mathrm{PDMS}}$) the value of $\log K_{O/W}$ is used to determine the recovery of a certain analyte. Using commercially available stir bars with PDMS volume of 124 μL, only analytes with $\log K_{O/W}$ of >3 can be extracted with a recovery higher than 80 % [26]. Because G and MG exhibit very low $\log K_{O/W}$ values (−0.69 and −0.58 for G and MG, respectively), extraction of G and MG with PDMS coating does not prove satisfactory. Therefore, derivatization was applied to convert the analytes into less polar bis-oximes ($\log K_{O/W}$ 3.40 and 3.69 for G-bis-BHA and MG-bis-BHA, respectively). The $\log K_{O/W}$ values were calculated using ALOGPS 2.1 [29, 30].

Previous experiments also revealed that the analytes in their underivatized form showed poor chromatographic separation on a reversed phase HPLC column and low ionization efficiencies during ESI [23]. Conversion into larger and less polar compounds improved chromatographic properties and ionization efficiencies.

The most frequently used derivatization reagent for carbonyl compounds in combination with LC is DNPH. DNPH is soluble only in diluted strong mineral acids, but strong acidic conditions may damage the stir bar's PDMS coating. Hence, the water-soluble derivatization reagents PFBHA (*O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine) and BHA (*O*-benzylhydroxylamine) were tested.

PFBHA is a common derivatization reagent for GC analyses and therefore available in high purity, which eliminates the need for purification. Nevertheless, both G and MG PFBHA-derivatives showed strong variations in ionization efficiency with unacceptably high relative standard deviation (RSD) values up to 60 % in triplicate measurements. Better results were obtained using BHA as derivatization reagent (RSD< 12 %), although purification is necessary because it is not commercially available in GC derivatization grade like PFBHA.

In the aqueous sample, the free form of G and MG is in equilibrium with hydrated monomeric and oligomeric forms. During derivatization, the derivatization reagent is used in excess (10,000 fold excess compared to a glyoxal concentration of 1 ng/mL) and under acidic conditions (pH 3.5) to ensure that the equilibrium is shifted towards the free monomeric form, which is accessible for the derivatization. That way, the measurements comprise the sum of free monomeric, hydrated, and reversibly formed higher oligomeric compounds [17, 31].

Time course of extraction and liquid desorption

Because SBSE is an equilibrium technique based on the partitioning of the analyte between the aqueous phase and the PDMS phase, the stirring times to reach equilibrium

during extraction and liquid desorption were determined. Different extraction times (1, 2, 5, 10, and 22 h) were tested for both G- and MG-bis-oximes. A stirring speed of 1,000 rpm was used and liquid desorption parameters were set as follows: stirring time 3 h, stripping solvent 1.5 mL ACN, stirring speed 500 rpm. As shown in Fig. 2a, in case of G, the equilibrium is reached after about 10 h, whereas for MG, a longer extraction time up to 22 h is needed. Therefore, an optimal extraction time of 20 h is used, which furthermore allows extraction overnight.

As the curve for the extraction of both analytes is similar, liquid desorption time was optimized using only MG. An extraction time of 20 h, stripping solvent of 1.5 mL ACN and stirring speed of 500 rpm was applied. Liquid desorption times of 0.5, 1, 2, 3, 4, 6, 8, and 20 h were tested. The equilibrium is reached after about 3 h with no significant change at longer stirring times, so 3 h is determined as optimal liquid desorption time (Fig. 2b).

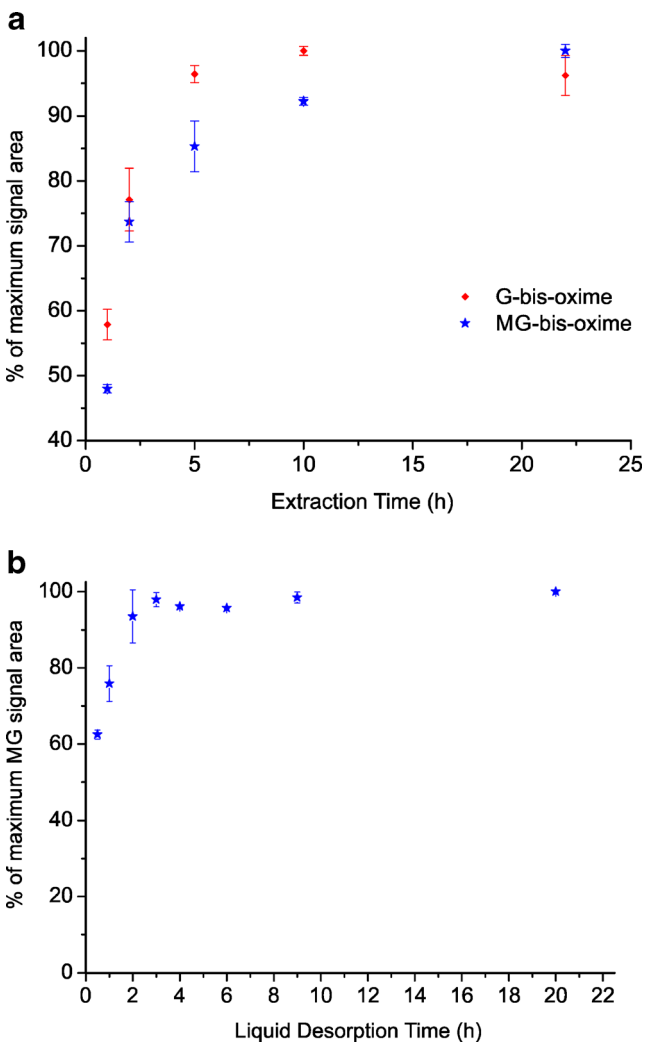

Fig. 2 Optimization of extraction time (**a**) and liquid desorption time (**b**)

Liquid desorption solvent

MeOH and ACN were tested as stripping solvents for liquid desorption. Using ACN, higher signal areas of the bis-oximes were obtained, therefore ACN was chosen as the stripping solvent in further optimization steps. A volume of 1.5 mL is needed to completely immerse the stir bar in the stripping solvent and to ensure that it is covered while stirring. For the same reason, the stirring speed was adjusted to 500 rpm during liquid desorption (instead of 1,000 rpm during extraction).

Additional optimization

Ionic strength and pH of the sample solution play an important role in the efficiency of the SBSE process. Derivatization is also influenced by pH which makes the process more complex. To ensure equal conditions for all samples and standards, they were acidified to a pH of about 3.5 with sulfuric acid prior to SBSE.

The influence of ionic strength on the extraction process was evaluated by adding 5–30 wt% NaCl to the aqueous sample solutions. No significant change in SBSE efficiency was observed. Therefore, no NaCl addition was applied in the method.

Sample volume

The effect of different sample volumes on extraction efficiency was determined by spiking a distinct volume of a standard solution containing G and MG to different volumes (5–70 mL) of ultrapure water. No significant differences in signal area were observed; hence, in the chosen volume range, the efficiency of the SBSE-LD process is independent of the sample volume, which can be adjusted depending on the expected concentration of the environmental sample.

Chromatographic separation and MS

The HPLC parameters were optimized for baseline separation and short retention times of G- and MG-bis-oximes. Separation was tested using C18, C8, and phenylhexyl columns. The best results based on peak shape and short retention time were obtained using a C8 column with gradient elution, heated to 30 °C.

Electrospray and MS parameters were optimized for maximum signal intensity in the positive mode. Selectivity of the detection was enhanced using MRM. During an MRM cycle, a targeted parent ion is isolated in the ion trap mass analyzer, followed by CID (helium as collision gas) and isolation of a particular daughter ion from the resulting fragmentation spectrum. This daughter ion is used for quantification. The same cycle is successively repeated for the three parent ions *m*/*z* 269

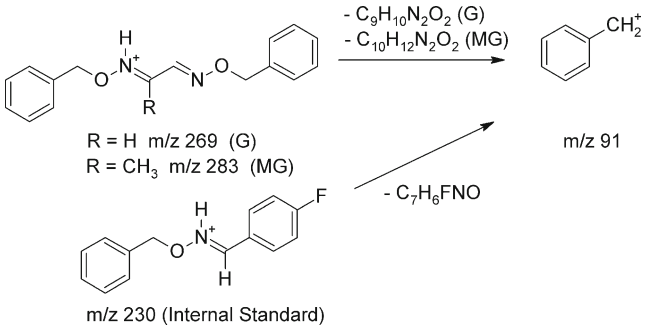

Fig. 3 Fragmentation of the precursor ions $[M + H]^+$ of the analytes G-bis-oxime and MG-bis-oxime and the internal standard oxime to yield the product ion used for quantification

(G), *m/z* 283 (MG), and *m/z* 230 (internal standard) multiple times during the chromatographic run. In initial MS/MS experiments, the fragment *m/z* 91 was identified as the most abundant product ion of both G- and MG-bis-oxime. Therefore *m/z* 269→*m/z* 91, *m/z* 283→*m/z* 91, and *m/z* 230→*m/z* 91 (for G, MG, and internal standard) were used as product ion transitions in MRM mode (see Fig. 3).

Validation

Calibration functions for G and MG were obtained by linear regression analysis. Calibration parameters are summarized in Table 1. To determine the instrumental limits of detection and quantification, the standard deviation of the blank samples (n=5) was multiplied by 3 and 10, respectively, and divided by the slope of the linear regression function. Instrumental limits of detection (ILOD) based on the amount of analyte in the liquid desorption extract were 242 and 213 pg/mL for G and MG. Method limits of detection and quantification based on a sample volume of 15 mL were 16 and 54 pg/mL for G and 14 and 47 pg/mL for MG, respectively.

To determine the recovery of the analytes, snow samples were spiked with G and MG at three different concentration levels (5–15 ng/mL) and analyzed in triplicate. The masses of the spiked samples were corrected by subtracting the masses of the unspiked snow sample and then compared to the nominal spiked masses. The results of the different spike levels were averaged to determine the recovery of the respective target compound. Recoveries were 78.9±5.6 % for G and 82.7±7.5 % for MG, respectively. Method inter-batch precision was evaluated by calculation the RSD in percent from different triplicate analyses of snow and ice samples measured on different days. A precision of 7.2±4.9 % for G and 11.4±5.9 % for MG was determined.

Application

The performance of the described method was tested by analyzing fresh snow samples from Hohenpeissenberg, southern Germany, and ice core samples from Upper Grenzgletscher in the southern Alps, Switzerland. G was detected in both snow samples and ice core samples and MG was detected in the snow samples and one of the ice core samples. Snow samples were collected from the surface and from a layer in 30 cm depth in triplicate with a meltwater sample volume of 5 mL used for analysis. Concentrations (corrected for recovery) were 16.3±1.2 ng/g (280.8±20.7 nM) for G and 3.5±0.4 ng/g (48.6±5.6 nM) for MG in the surface snow samples. Similar concentrations were found in the layer 30 cm below the surface (15.4±1.4 ng/g for G and 3.6±0.3 ng/g for MG, respectively), indicating no age difference between the two layers. The obtained concentrations are in the same order of magnitude as concentrations reported in other field studies from urban and rural areas: 200–7100 nM for G and 30–60 nM for MG ([32], sampled in southern California), 44.8 and 25.0 nM for G and MG in Tokyo snow ([21], converted from micrograms per liter values). Concentrations reported in this study are one order of magnitude higher than those found in remote, polar areas, i.e., 13.9 and 6.9 nM for G and MG in Greenland Snow ([21]) and 13.9–37.1 and 1.9–6.5 nM for G and MG in surface snow from Barrow, Alaska ([17]). This can be explained by the much longer distance between polar regions and possible emission regions of G and MG or their precursors.

Ice core samples from two different years (sample 1: 1959, sample 2: 1991) were analyzed. Resulting concentrations were 0.178 ng/g (3.06 nM) for G and 0.126 ng/g (1.75 nM) for MG in sample 1 and 0.085 ng/g (1.46 nM) for G in sample 2 with MG below detection limit. The meltwater sample volume used for analysis was 15 mL. The concentration values are in the same order of magnitude as reported in a field study focusing on the chemical composition of a Greenland ice core (0.023–1.14 ng/g for G and 0.031–1.36 ng/g for MG, [19]).

The concentrations measured in the ice core are much lower (almost two orders of magnitude for G) than the

Table 1 Calibration data

	Slope[a]	Intercept[a]	R^2	Recovery (%)	ILOD (ng/mL)	ILOQ (ng/mL)
G	0.037	−0.018	0.9988	78.9±5.6	0.242	0.807
MG	0.025	−0.034	0.9941	82.7±7.5	0.213	0.711

[a] Determined using the measured signal area quotient (analyte/internal standard)

concentrations in the fresh snow samples. Obviously, as this is only a limited dataset, it is not possible to draw reliable conclusions regarding the fate of G and MG in the snow or ice samples; however, the described analyses show the good applicability of the method to the given issue of detecting small and even trace amounts of G and MG in snow and ice core samples.

Conclusions

We have described the development and optimization of a new, sensitive, and selective method using stir bar sorptive extraction with liquid desorption and HPLC-MS/MS to quantify the alpha-dicarbonyls glyoxal and methylglyoxal in molten ice and snow. Key SBSE parameters such as extraction and liquid desorption time, derivatization, salt addition, and desorption solvent were optimized. Method detection limits were in the low picogram per milliliter range. The method was successfully applied to snow and ice core samples from the Alpine region. For snow samples, a sample volume of only 5 mL is sufficient; for less concentrated samples like ice cores, the sample volume can be adjusted to larger volumes (i.e., 15 mL) without loss of extraction efficiency.

Analyses of snow samples from different depth and location may give hints for the interaction of G and MG between snow and atmosphere. A larger dataset is needed improve the understanding of the complex processes occurring in the snowpack. Historic records of G (and MG) in ice cores can give hints concerning the oxidative capacity of the atmosphere, as the analytes are tracers of VOC oxidation chemistry and SOA. Besides, ice core data may be of great benefit especially in connection with other marker compounds of biogenic and anthropogenic origin to get information on qualitative and quantitative changes of emission sources over time.

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