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Atmospheric Measurement Techniques Discussions

Characterisation and optimisation of a method for the detection and quantification of atmospherically relevant carbonyl compounds in aqueous medium

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Abstract

Carbonyl compounds are ubiquitous in the atmosphere and either emitted primarily from anthropogenic and biogenic sources or they are produced secondarily from the oxidation of volatile organic compounds (VOC). Despite a number of studies about the quantification of carbonyl compounds a comprehensive description of optimised methods is scarce for the quantification of atmospherically relevant carbonyl compounds. Thus a method was systematically characterised and improved to quantify carbonyl compounds. Quantification with the present method can be carried out for each carbonyl compound sampled in the aqueous phase regardless of their source. The method optimisation was conducted for seven atmospherically relevant carbonyl compounds including acrolein, benzaldehyde, glyoxal, methyl glyoxal, methacrolein, methyl vinyl ketone and 2,3-butanedione. O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) was used as derivatisation reagent and the formed oximes were detected by gas chromatography/mass spectrometry (GC/MS). The main advantage of the improved method presented in this study is the low detection limit in the range of 0.01 and 0.17 µmol L^{-1} depending on carbonyl compounds. Furthermore best results were found for extraction with dichloromethane for 30 min followed by derivatisation with PFBHA for 24 h with 0.43 mg mL^{-1} PFBHA at a pH value of 3. The optimised method was evaluated in the present study by the OH radical initiated oxidation of 3-methylbutanone in the aqueous phase. Methyl glyoxal and 2,3-butanedione were found to be oxidation products in the samples with a yield of 2 % for methyl glyoxal and 14 % for 2,3-butanedione.

1 Introduction

Carbonyl compounds are ubiquitous in the atmosphere and they play an important role in the atmospheric gas- and particle phase chemistry (Grosjean, 1982). They are directly emitted from both biogenic and anthropogenic sources (Carlier et al., 1986)

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and they can be formed secondarily during the oxidation of volatile organic compounds (VOC) (Hallquist et al., 2009). According to the literature, carbonyl compounds represent 79 and 89 % of the alkane and alkene oxidation products in the presence of NO_x, respectively (Calvert and Madronich, 1987). Depending on their Henry constants carbonyl compounds partition into the aqueous phase and due to their high solubility in water they can undergo multiphase reactions (Ravishankara, 1997). Reactions in the aqueous phase can be divided into radical reactions (Herrmann et al., 1999) and non-radical reactions such as aldol condensation (Loeffler et al., 2006) leading to various multifunctional products.

Numerous methods exist to detect and quantify carbonyl compounds in atmospheric samples. These methods can be categorised into spectroscopy based techniques such as differential optical absorption spectroscopy (DOAS, Platt et al., 1979), Fourier transform infrared spectroscopy (FT-IR, Tuazon et al., 1978) and mass spectrometry based (MS) techniques such as online proton transfer reaction mass spectrometry (PTR-MS), offline gas chromatography coupled to mass spectrometry (GC/MS) and liquid chromatography coupled to mass spectrometry (LC/MS). For the GC/MS and LC/MS techniques carbonyl compounds often require a derivatisation step prior the analysis. Among several derivatisation reagents 2,4-dinitrophenylhydrazine (DNPH, Lowe et al., 1980) and o-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) are most commonly used for the analysis of atmospheric carbonyl compounds.

In the present study, thorough characterisation of a PFBHA based derivatisation method was performed and an improvement was made to achieve a better quantification of atmospheric relevant carbonyl compounds in aqueous samples which might origin from fog, cloud and rain samples. Furthermore, such samples can also be formed from gas phase sampling into aqueous solutions by mist chambers (Seaman et al., 2006) and impinger samples (Lelacheur et al., 1993) or by partitioning sampling techniques such as C-GIS (condensation-growth and impaction system; Sierau et al., 2003), MARGA (Monitor for Aerosols and Gases in Air; ten Brink et al., 2009)

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and PILS (particle into liquid sampler; Sorooshian et al., 2006). The carbonyl compounds investigated in the present study were acrolein, methacrolein, methyl vinyl ketone, benzaldehyde, glyoxal, methyl glyoxal and 2,3-butanedione. These compounds were chosen because of their atmospheric relevance. Acrolein is emitted from incomplete combustion (Seaman et al., 2009) and formed during the oxidation of volatile organic compounds (1,3-dienes) with a mixing ratio between 0.13 and 7 ppb in ambient atmosphere (Altshuller, 1983). This compound has an adverse health effect leading to asthma and other chronic lung diseases (Leikauf, 2002). Methacrolein and methyl vinyl ketone are the major first generation oxidation products of isoprene (Kroll et al., 2006). They are suggested to be precursor compounds for glyoxal and methyl glyoxal in the atmospheric aqueous phase. In addition to isoprene oxidation glyoxal and methyl glyoxal are produced in the oxidation of a variety of VOCs (Fu et al., 2008). Due to their high water solubility they partition into the atmospheric aqueous phase, acting as precursor compounds for the formation of secondary organic aerosol (Ervens and Volkamer, 2010). Benzaldehyde can be formed in oxidation of aromatic VOCs such toluene and mixing ratios in the range of higher ppb levels in polluted regions are reported (Jang and Kamens, 2001). The oxidation of aromatic VOCs also forms 2,3-butanedione (Atkinson and Aschmann, 1994; Schütze and Herrmann, 2004). As this compound can be found in the aqueous phase 2,3-butanedione was used as a standard compound for the method improvement.

2 Experimental

2.1 Sample preparation

150 µL of the internal standard (cyclohexanone-2,2,6,6-d4, 0.049 mol L^{-1}) was added to 3 mL of the aqueous standard solution. The solution contains the following seven authentic standard compounds: acrolein, benzaldehyde, glyoxal, methyl glyoxal, methacrolein, methyl vinyl ketone and 2,3-butanedione (8 µmol L^{-1} each). For derivati-

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sation a PFBHA concentration of 0.43 mg mL^{-1} was prepared and allowed to rest for 24 h at room temperature. Then, the sample was acidified with hydrochloric acid (37 %) to pH = 1 and the mixture was shaken with an orbital shaker for 30 min (1500 rpm, revolutions per min). A 250 µL aliquot of dichloromethane was added to the mixture to extract the analytes and 1 µL of the organic phase was injected into GC. For further information about the experimental procedure see Supplement S1.

3 Results

In Table 1 an overview is given about existing method optimisations for the quantification of carbonyl compound with a prior PFBHA derivatisation step. Since numerous studies exist dealing with PFBHA derivatisation of carbonyl compounds only those methods are included in Table 1 which (i) derivatise carbonyl compounds in the aqueous phase (derivatisation on solid phase, cartridges or on a chip are not compared: Cullere et al., 2004; Nawrocki et al., 1996; Pang et al., 2013), (ii) optimise one of the investigated reaction parameters and (iii) use the same extraction techniques as in the present study (solid phase micro extraction or extraction on fibre are not included, e.g. Cancho et al., 2002). Therefore studies which also optimised a PFBHA method but do not fulfil the selection criteria (i)–(iii) are not included. Additionally, in Table S1 (Supplement S2.1) the application of the optimised methods is summarised.

Overall the derivatisation methods summarised in Table 1 are not comprehensively optimised. Therefore derivatisation parameters like extracting reagent or reaction time have to be improved to achieve an optimal derivatisation of carbonyl compounds and better detection limits. To improve commonly used PFBHA methods a mixture of seven standard compounds (acrolein, methacrolein, methyl vinyl ketone, glyoxal, methyl glyoxal, benzaldehyde, 2,3-butanedione) was used and the method optimisation was conducted with a stock solution of 8 µmol L^{-1}. During the derivatisation, (*E*) and (*Z*)-isomers of the derivatives are formed and this leads to two peaks in the chromatogram (Glaze et al., 1989). As the ratios of the peak areas for (*E*) and (*Z*)-isomers were found

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to stay constant, one peak per compound was considered for the method optimisation. Optimised parameters for the derivatisation procedure include the extracting reagent, extraction and derivatisation time, the amount of PFBHA and pH value before and after derivatisation (Table 2).

3.1 Extracting reagent

Dichloromethane, toluene, hexane, isooctane and chloroform were tested as extracting reagents. Figure 1 illustrates the influence of the extracting reagent on the amount of detected carbonyl compounds. Surprisingly, from the comparison dichloromethane turned out as the most effective extracting reagent. This is in contrast to former studies where hexane was commonly used as extracting reagent (EPA method 556; Glaze et al., 1989; Lelacheur et al., 1993; Seaman et al., 2006; Serrano et al., 2013). Besides hexane dichloromethane and chlorobenzene were also found as good extracting reagents (Spaulding and Charles, 2002; Ye et al., 2011). In the present study hexane resulted in lower peak areas of the carbonyl compounds due to less effective extraction. In turn this underestimation leads to a higher detection limit compared to the other extraction reagents (Table 3). The detection limits were determined for the present study in the single ion mode (SIM) based on a signal to noise ratio (S/N) of ≥ 3 and compared to those reported by Glaze et al. (1989). Note, 5.6 mL of the sample was extracted with 1 mL hexane resulting in a preconcentration factor of ≈ 6 (Glaze et al., 1989). In the present study a preconcentration factor of ≈ 12 was reached. In the case of acrolein the detection limit was found to be improved by a factor of ≈ 2. The detection limit of other compounds investigated in this study showed an improvement by about a factor of 10 compared to Glaze et al. (1989). Further comparison of detection limits can be found in the Supplement S2.2. Based on these results dichloromethane was chosen as extracting reagent.

Furthermore, in the literature toluene is also recommended as extracting reagent (Strassnig et al., 2000). This can be confirmed at least for the extraction of benzalde-

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hyde. The better extraction of benzaldehyde with toluene is likely due to the aromatic character of both toluene and benzaldehyde.

3.2 Extraction time

In addition to the extracting reagent, it was found that the extraction time had a significant influence on the quantity of the extracted derivatised carbonyl compounds (Fig. S1; Supplement S2.3). It was found that the integrated peak areas increase with an increasing extraction time. An extraction time less than 15 min was not sufficiently long enough to extract the target analytes completely. To ensure the complete extraction of the analytes, the extraction time was extended to 30 min, and the extraction procedure was repeated three times. After the first extraction the amount of detected oxime was negligibly small (≈ 2 %, Table S2; Supplement S2.3) indicating an almost complete extraction within 30 min. This is contradicting to the literature with 2 min (Ye et al., 2011) and 3 min extraction time (EPA method 556). However, the data set on the influence of the extraction time is scarce and no further method development was found in the literature examining this issue. Furthermore most of studies in the past used very short extraction times (e.g. Glaze et al., 1989; Lelacheur et al., 1993; Serrano et al., 2013). These shorter extraction times likely cause significant lower peak areas of the oximes and therefore higher detection limits. Based on the data obtained in the present study, an extraction time of 30 min and dichloromethane as an extracting reagent can be recommended. Because hexane is the commonly used extraction reagent different extraction times were tested for hexane. Based on this, correction factors were determined to enable the comparison of the newly optimised method to the established hexane method (see Supplement S2.3).

3.3 Derivatisation time

The influence of the derivatisation time was evaluated by reacting carbonyl compounds with PFBHA for a duration ranging from 0.5 to 48 h (Fig. S3, Supplement S2.4). For

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all the investigated carbonyl compounds it was found that the reaction was almost completed after 24 h. Thus, it is recommended to use a derivatisation time of 24 h in good agreement to the findings by Lelacheur et al. (1993) and Kobayashi et al. (1980). Nevertheless, optimised derivatisation times can be found ranging from 20 s to 96 h (EPA method 556; Glaze et al., 1989; Hudson et al., 2007; Kobayashi et al., 1980; Lelacheur et al., 1993; Saison et al., 2009; Seaman et al., 2006; Serrano et al., 2013; Strassnig et al., 2000; Sugaya et al., 2004; Takeuchi et al., 2007). Among several compounds investigated in the cited studies formaldehyde, acetaldehyde, butanal, methyl ethyl ketone and methyl butyl ketone were used (Glaze et al., 1989). In the study by Glaze et al. (1989) an optimal derivatisation time of 2 h for aldehydes was found but much longer derivatisation times were identified for ketones. The difference between that study and the results obtained within the present study might be caused by the carbonyl compounds used for the optimisation. Only small, saturated aldehydes like acetaldehyde were used during the investigations of Glaze and co-workers whereas much larger carbonyl compounds were used in the present study. It can be expected that the molecule size has also an influence on the optimal derivatisation time and this might explain the observed differences. Nevertheless, similar a shorter derivatisation time can be found as well in literature whereby an optimal result was obtained after 2 and 4 h of derivatisation for acetone and formaldehyde (Hudson et al., 2007; Takeuchi et al., 2007). Furthermore, shorter derivatisation times were reported when higher temperatures (EPA method 556; Serrano et al., 2013; Sugaya et al., 2004) or microwave-assisted derivatisation (Strassnig et al., 2000) were applied.

Contrary, longer derivatisation times of 24 to 96 h were observed as an optimal result by Seaman et al. (2006). They reported that glyoxal and methyl glyoxal needed longer derivatisation times due to their two carbonyl groups. Furthermore, the carbonyl compounds were sampled and derivatised in a sodium bisulfite solution. After the carbonyl-bisulfite adduct was formed hydrogen peroxide was added to destroy the formed adduct and to yield carbonyl compounds which were directly derivatised with

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PFBHA. These steps were conducted simultaneously which might cause the longer derivatisation times.

3.4 Amount of PFBHA in the derivatisation

To investigate the influence of the amount of derivatisation reagent, PFBHA concentration in the sample solution was varied from 0.09 to 1.72 mg mL^{-1} (Fig. S4, Supplement S2.5). The optimum was reached at 0.43 mg mL^{-1} whereas a decrease in the oxime formation can be observed over this concentration. Based on this result, the PFBHA concentration was set to 0.43 mg mL^{-1}. Such a decrease has been reported in the literature examining acrolein, glyoxal and methyl glyoxal which is explained by a less effective extraction of the oxime due to an increasing amount of PFBHA in the organic phase (Saison et al., 2009). In a number of studies an optimisation of the PFBHA concentration cannot be found (Glaze et al., 1989; Hudson et al., 2007; Lelacheur et al., 1993; Spaulding and Charles, 2002; Sugaya et al., 2004) as only few studies exist examining this issue (EPA method 556; Kobayashi et al., 1980; Saison et al., 2009; Seaman et al., 2006; Serrano et al., 2013; Strassnig et al., 2000; Ye et al., 2011). Nevertheless, 0.43 mg mL^{-1} found in the present study are in good agreement to a study by Serrano et al. (2013) which recommended 0.3 mg mL^{-1}. Even if much lower PFBHA concentrations were found to be optimal a much higher PFBHA concentration was used to ensure a complete derivatisation. Despite these facts two studies exist which found much lower PFBHA concentration of 0.1 and 0.05 mg mL^{-1} as optimal (Kobayashi et al., 1980; Ye et al., 2011). They investigated only saturated carbonyl compounds which could be a reason for the lower PFBHA amount. Furthermore Strassnig et al. (2000) optimised the PFBHA amount concluding the best PFBHA amount is 0.8 mg mL^{-1} which is two times higher than the optimal PFBHA amount found in this study. It should be mentioned that the derivatisation was conducted in a microwave oven therefore the derivatisation occurred under other conditions than in this study. Furthermore for the derivatisation of the carbonyl compound with the EPA

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method 556 also a higher PFBHA amount of 0.75 mg mL^{-1} is used. This finding cannot be compared because the derivatisation was carried out at a temperature of 35 °C.

3.5 pH value during derivatisation and extraction

The pH value was varied between pH = 1 and pH = 7 with hydrochloric acid and sodium hydroxide for the investigation of the influence of the pH value on the quantification of the carbonyl compounds. The pH value can be varied for two experimental steps, first the pH value of the derivatisation reaction (Fig. S5, Supplement S2.6) and second the extraction of the oxime (Fig. S6, Supplement S2.6). No influence of the pH value on the derivatisation step was observed (Fig. S5). Based on this a pH value of 3 was chosen because this requires no further addition of hydrochloric acid or sodium hydroxide and second, it was found that at pH = 3 the SD was lower. After the derivatisation with PFBHA the oxime is extracted with dichloromethane. This step was also found to be not pH dependent (Fig. S6). However, under highly acidic conditions a smaller fraction of PFBHA was found in the organic phase. The smaller fraction of PFBHA might be caused by a less pronounced phase transfer of PFBHA in the organic phase when the aqueous phase was acidified to pH = 1 (Yu et al., 1995). Therefore the pH value for the extraction of the oxime was set to pH = 1 as it minimises the amount of PFBHA in the organic phase and thus in the chromatogram.

3.6 Evaluation of the optimised method and application

The optimised method (dichloromethane as extracting reagent, 30 min extraction time, 24 h derivatisation time, 0.43 mg mL^{-1} PFBHA, pH = 3 for the derivatisation and pH = 1 for the extraction) was applied to a series of stock solutions containing seven target carbonyl compounds in the range of 2 to 16 µmol L^{-1} (Fig. S7, Supplement S2.7). From the repetitive analysis of the dilution series a R^2 of 0.99 and detection limits between 0.01 and 0.17 µmol L^{-1} were achieved (Table 3).

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The optimised method was evaluated to detect and quantify carbonyl compounds formed during the oxidation of 3-methylbutanone with OH radicals in the aqueous solution. Among numerous oxidation products methyl glyoxal and 2,3-butanedione (Fig. 2a) were positively identified and quantified with the developed method. Methyl glyoxal and 2,3-butanedione could not be detected at the beginning of the experiment (Fig. 2b). After one hour the peak areas of the carbonyl compounds start to increase as they are formed by the reaction. For both compounds two peaks were found corresponding to (*E*) and (*Z*)-isomers of the oximes (Glaze et al., 1989). The reaction was stopped after 5 h and the products were quantified with authentic standard compounds. The determined concentrations were 2.1 µmol L^{-1} for methyl glyoxal and 13.6 µmol L^{-1} for 2,3-butanedione after five hours. This corresponds to a yield of 2 % for methyl glyoxal and 14 % for 2,3-butanedione.

4 Summary

The present study showed that dichloromethane gives a better recovery of the oximes compared to the commonly used hexane for the derivatisation of carbonyl compounds with PFBHA in aqueous solution. Furthermore the extraction time was set to 30 min which corresponds to an increase by a factor of up to 60 compared to previously published methods (e.g. Glaze et al., 1989). Furthermore the derivatisation time was increased by a factor of up to 12 (Glaze et al., 1989). The improvement enabled a much better detection limit between 0.01 and 0.17 µmol L^{-1} for seven carbonyl compounds tested in this study. In addition the derivatisation time was set to 24 h to complete the derivatisation of carbonyl compounds bearing a keto group. To investigate the effect of the amount of derivatisation reagent, different PFBHA concentrations were added and the best result was found at a concentration of 0.43 mg mL^{-1}.

The optimised method was applied to detect carbonyl compounds formed during the oxidation of 3-methylbutanone in aqueous phase namely methyl glyoxal and 2,3-butanedione. The results obtained from the analysis of laboratory produced samples

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showed that the developed method is suitable for the detection and quantification of carbonyl compounds in aqueous samples, especially in low quantities.

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Table 1. References optimised the PFBHA derivatisation. The optimised method parameters are given in bold and the parameters matching with the present study are underlined.

PFBHA [mg mL^{-1}]	Derivatisation time	Extracting reagent	Extraction time [min]	Matching compounds and detection limits [µmol L^{-1}]	Reference
0.1	**40 min, 24 h for ketones**	Ethyl acetate	–	–	Kobayashi et al. (1980)
0.1	**2 h (longer for ketones)**	Hexane	0.5	Acrolein (0.3) Benzaldehyde (0.1) Glyoxal (0.1) Methyl glyoxal (0.1)	Glaze et al. (1989)
> 10 fold excess	**24 h**	Hexan, Methyl*tert*-butyl ether	1	Glyoxal	Lelacheur et al. (1993)
0.8	**20 seconds (900 W)**	Toluene	–	Benzaldehyde	Strassnig et al. (2000)
0.5	24 h	**Dichloro-methane**	–	–	Spaulding and Charles (2002)
0.06	**4 h (60 °C)**	–	–	–	Sugaya et al. (2004)
0.2	**24–96 h**	Hexane	–	Acrolein (1.2×10^{-2}–3.5×10^{-2} µg m^{-3}) Methacrolein (7.0×10^{-2}–3.3×10^{-2} µg m^{-3}) Methyl vinyl ketone (3.8×10^{-2}–5.0×10^{-2} µg m^{-3}) Glyoxal (5.0×10^{-2}–21.6×10^{-2} µg m^{-3}) Methyl glyoxal (2.9×10^{-2}–3.8×10^{-2} µg m^{-3}) Benzaldehyde (2.0×10^{-2}–4.4×10^{-2} µg m^{-3})	Seaman et al. (2006)
0.06	**2 h**	–	–	–	Hudson et al. (2007)
–	**4 h**	–	–	–	Takeuchi et al. (2007)
0.75	**10 min**	–	–	Benzaldehyde Methyl glyoxal 2,3-Butanedione	Saison et al. (2009)
0.05	< 10 min	**Chloro-benzene**	**2**	–	Ye et al. (2011)
0.5	**1 min (60 °C)**	**Hexane**	1	Benzaldehyde (0.1×10^{-3}) Methyl glyoxal (0.01×10^{-3}) Glyoxal (0.01×10^{-3})	Serrano et al. (2013)
0.75	2 h (35 °C)	Hexane	3	Benzaldehyde (0.003) Glyoxal (0.01) Methyl glyoxal (0.01)	EPA method 556
0.4	***24 h***	***Dichloro-methane***	***30***	*Acrolein (0.17)* *Methacrolein (0.02)* *Methyl vinyl ketone (0.03)* *Benzaldeyhde (0.01)* *Glyoxal (0.01)* *Methyl glyoxal (0.1)* *2,3-Butanedione (0.1)*	*This work*

Optimised parameters given in bold; matching parameters are underlined.

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Table 2. Overview about the investigated parameters. The optimal parameters found in the present study are given in bold.

Parameter	Range	Number of repetitions
Extracting reagent	**Dichloromethane**	3
	Toluene	3
	Hexane	3
	Isooctane	3
	Chloroform	3
Extraction time	5, 15, **30**, 60 min	3
Derivatisation time	0.5, 1, 2, 6, **24**, 48 h	3
Added amount of PFBHA	0.09, 0.22, **0.43**, 0.86, 1.72 mg mL^{-1}	3
pH value (Derivatisation)	pH = 1, **3**, 5, 7	3
pH value (Extraction)	pH = **1**, 3, 5, 7	3

Selected parameters given in bold.

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Table 3. Detection limits of the carbonyl compounds determined with GC/MS (SIM).

Carbonyl compound	Detection limit [µmol L^{-1}] S/N ≥ 3, $n = 3$
Acrolein	0.17
Methacrolein	0.02
Methyl vinyl ketone	0.03
Benzaldehyde	0.01
Glyoxal	0.01
Methyl glyoxal	0.01
2,3-Butanedione	0.01

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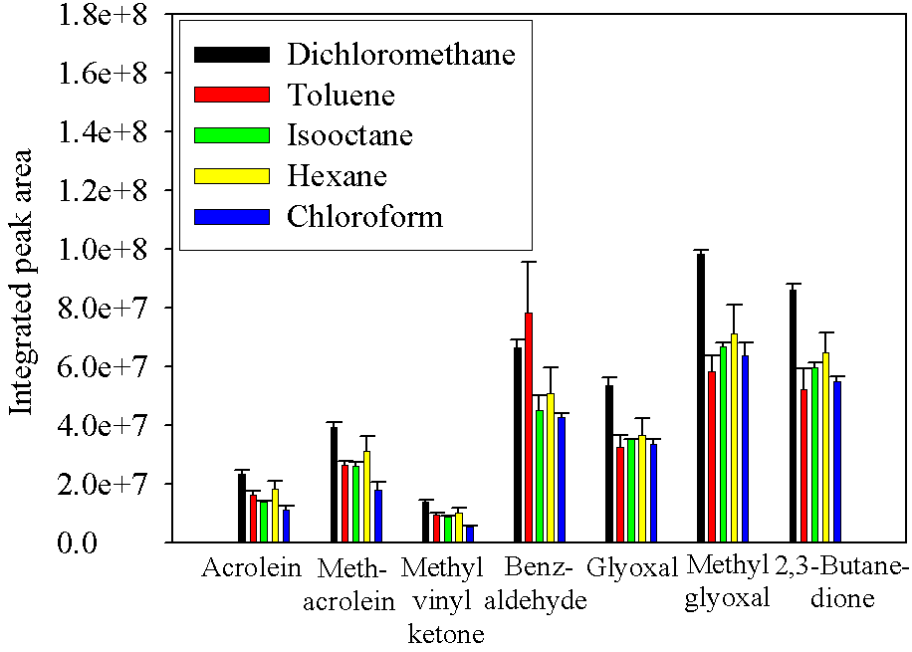

Figure 1. Influence of the extracting reagents dichloromethane (black), toluene (red), isooctane (green), hexane (yellow) and chloroform (blue) on the integrated peak areas of the standard compounds acrolein, methacrolein, methyl vinyl ketone, benzaldehyde, glyoxal, methyl glyoxal and 2,3-butanedione.

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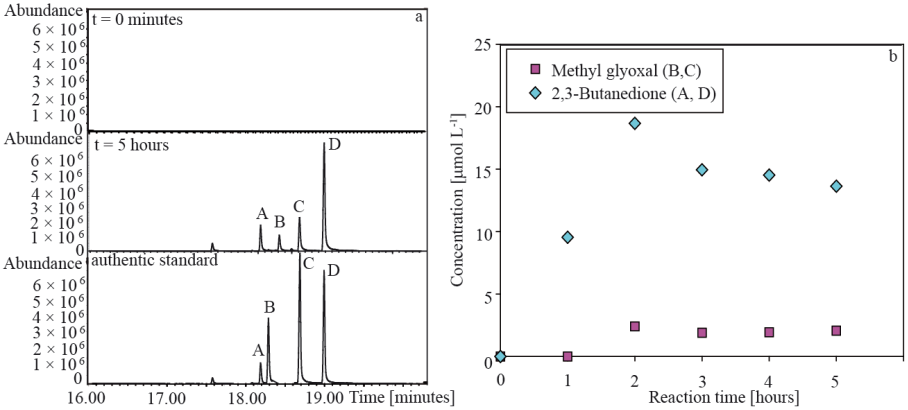

Figure 2. GC/MS chromatogram of time resolved formation of 2,3-butanedione (A,D) and methyl glyoxal (B,C) during the oxidation of 3-methylbutanone (starting time $t = 0$ h and reaction time $t = 5$ h) and the GC/MS chromatogram of the authentic standards **(a)**. Calculated concentrations of the formed products 2,3-butanedione and methyl glyoxal over the entire run of the experiment **(b)**.

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