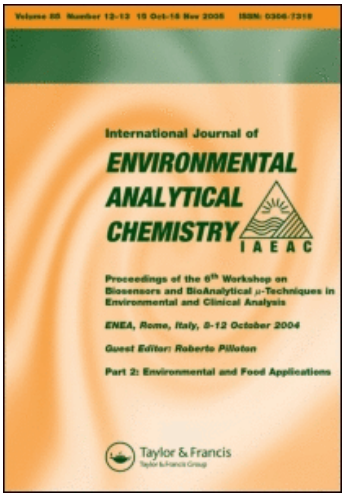

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Development of a highly sensitive method for determining atmospheric carbonyl compounds by passive sampling and application of the method to a survey of indoor air

Masahiro Fusaya[a]; Takeshi Ohura[b]; Morimasa Suzuki[a]; Takashi Amagai[b]; Hidetsuru Matsushita[a]
[a] Shizuoka Institute of Environment and Hygiene, 4-27-2 Kita-ando, Shizuoka 420-8637, Japan [b] Institute for Environmental Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422-8526, Japan

To cite this Article Fusaya, Masahiro , Ohura, Takeshi , Suzuki, Morimasa , Amagai, Takashi and Matsushita, Hidetsuru(2004) 'Development of a highly sensitive method for determining atmospheric carbonyl compounds by passive sampling and application of the method to a survey of indoor air', International Journal of Environmental Analytical Chemistry, 84: 14, 1035 — 1044
To link to this Article: DOI: 10.1080/03067310412331303190
URL: http://dx.doi.org/10.1080/03067310412331303190

Intern. J. Environ. Anal. Chem.
Vol. 84, No. 14–15, pp. 1035–1044, 10 December–20 December 2004

DEVELOPMENT OF A HIGHLY SENSITIVE METHOD FOR DETERMINING ATMOSPHERIC CARBONYL COMPOUNDS BY PASSIVE SAMPLING AND APPLICATION OF THE METHOD TO A SURVEY OF INDOOR AIR

MASAHIRO FUSAYA[a], TAKESHI OHURA[b,*], MORIMASA SUZUKI[a], TAKASHI AMAGAI[b] and HIDETSURU MATSUSHITA[a]

[a]*Shizuoka Institute of Environment and Hygiene, 4-27-2 Kita-ando, Shizuoka 420-8637, Japan;*
[b]*Institute for Environmental Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422-8526, Japan*

(Received 28 May 2004; In final form 25 July 2004)

A simple, highly sensitive analytical method for measuring many kinds of carbonyls in air using a passive sampler containing a sorbent (silica gel) coated with 2,4-dinitrophenylhydrazine has been developed. The carbonyls collected by the sampler were extracted with a solvent, and the extracts were subjected to high-performance liquid chromatography (HPLC; UV detection) without first being concentrated. In this method, the volume injection is examined, and is found to have a sensitivity at least 20 times that of ordinary HPLC methods. The air concentrations of nine carbonyls collected by passive sampling over a period of 24 h were estimated by means of conversion equations derived from the results of active sampling; $c = 10^{[\log(y)-b]/a}$, where c is the carbonyl concentration in air ($\mu g/m^3$); y is the amount of carbonyl collected by the passive sampler (μg); and a and b are constants for each carbonyl compound. The calculated air concentrations were consistent with the concentrations measured by active sampling. This method may be useful in determining personal exposure to ambient carbonyls.

Keywords: Passive sampling; Formaldehyde; Carbonyl compounds; Indoor air; HPLC

INTRODUCTION

Various carbonyl compounds, including formaldehyde, acetaldehyde, and acrolein, are known to be toxic, mutagenic, and/or carcinogenic, and, as a result, have been identified as hazardous air pollutants [1]. Carbonyl compounds are also an important source of radicals in the chemistry of ozone production [2–4]. Formaldehyde and acetaldehyde damage the eyes, nose, and respiratory organs, and cause allergies and what is known as 'sick house syndrome'. In Japan, indoor air guidelines set the allowed values for formaldehyde and acetaldehyde at 100 and 48 $\mu g/m^3$, respectively [5–7]. Six acetaldehydes,

* Corresponding author. Fax: +81-54-264-5798. E-mail: ooura@smail.u-shizuoka-ken.ac.jp

ISSN 0306-7319 print: ISSN 1029-0397 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/03067310412331303190

propionaldehyde, *n*- and *i*-butylaldehyde, and *n*- and *i*-valeraldehyde, have been designated as offensive odour substances in Japan [8]. Therefore, the determination of the occurrences of various species of carbonyl compounds, in addition to formaldehyde and acetaldehyde, in air is important for assessing the health risks of exposure.

The prevailing method for sampling carbonyls in air is an active sampling method that utilizes a solid sorbent (silica gel) coated with 2,4-dinitrophenylhydrazine (DNPH) as the medium on which carbonyl compounds are collected as DNPH derivatives [9–17]. The greatest merit of active sampling is that sufficient air volumes for analysis of carbonyl compounds are obtained, so that the sampling times can be relatively short (~24 h). Surveys of carbonyl compounds using active samplers have been conducted in indoor and outdoor air all over the world [18–26].

Passive samplers are also used to collect certain carbonyl compounds. Passive samplers have several advantages over active samplers because the former can be used where electricity is not available, and they are small, light, and silent, which is especially important for measuring personal exposure and analysing indoor air. In addition, field validation is unnecessary, the concentration is integrated continuously without interruption, and the samplers can be produced at a low cost. However, their applications have been limited to carbonyl compounds present in relatively high concentrations, such as formaldehyde, because the sampling rates are low compared with active sampling rates [27–30]. Therefore, long-term sampling (>72 h) is generally needed to investigate carbonyl compounds present at relatively low concentrations in air.

We have developed an analytical technique for passive sampling within 24 h to measure 16 species of carbonyl compounds in the air, and we have confirmed the adjustability of the technique by using it to survey indoor air.

EXPERIMENTAL

Chemicals

DNPH derivatives of 16 carbonyl compounds (formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, *i*- and *n*-butylaldehyde, crotonaldehyde, *i*- and *n*-valeraldehyde, benzaldehyde, hexaldehyde, *o*-, *m*-, and *p*-tolualdehyde, and 2,5-dimethylbenzaldehyde) were purchased from Tokyo Kasai Kogyo (Tokyo, Japan) and used without purification. The standards were dissolved in HPLC-grade acetonitrile (Wako Chemicals, Osaka, Japan). The dichloromethane used for extraction was pesticide-residue-analysis grade (Wako Chemicals, Osaka, Japan); and the dimethyl sulfoxide (DMSO) and water used for sample preparation were fluorometric-analysis grade (Wako Chemicals, Osaka, Japan) and HPLC grade (Wako Chemicals, Osaka, Japan), respectively.

Sampling

To develop a method for measuring multicomponent mixtures of carbonyl compounds in air by passive sampling, we used a DNPH-coated passive sampler (Sibata Scientific Technology Ltd, Tokyo, Japan; Fig. 1). The air concentrations for individual carbonyl compounds collected by passive sampling were calculated from the results of simultaneous measurements by active and passive samplers. The active sampler consisted

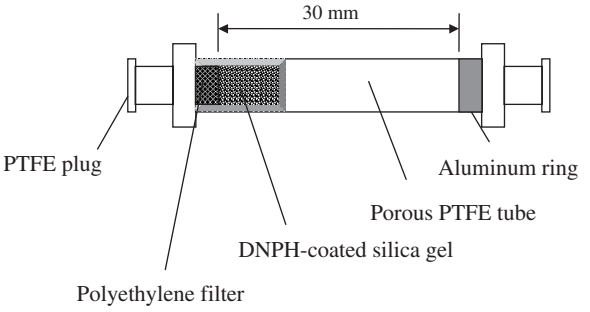

FIGURE 1 Schematic of the passive sampler.

of a Waters Sep-Pak XpoSure cartridge (Waters Co., Milford, MA) and a mini-pump (MP-15CFH, Sibata Scientific Technology Ltd, Tokyo) at a flow rate of 200 mL/min. After sampling was conducted for a predetermined time, the samplers were stored at −20°C in sealed aluminium bags until extraction. The surveys of indoor air by means of the passive sampler were performed for 24 h in restrooms ($n = 3$), a library ($n = 1$), and an office ($n = 1$) in the Shizuoka Institute of Environment and Hygiene. The indoor temperature during the surveys ranged from 10 to 20°C. No smokers were present in the rooms during the surveys.

Analytical Method

The sampled material was eluted from the sampler in a 15-mL glass tube with 6.0 mL of dichloromethane. DMSO (30 μL) was then added to the tube to preserve the carbonyls, and the solvent was evaporated under a N_2 stream. The residues were dissolved in 300 μL of acetonitrile, and then 670 μL of water was added. The target carbonyl compounds were analysed with an HPLC system consisting of an LC-10Avp series chromatograph (Shimadzu Co., Kyoto, Japan) and a photodiode array detector (SPD-M10Avp, Shimadzu Co., Kyoto, Japan) at 360 nm. A Wakosil-DNPH (Wako Chemicals) column (4.6 mm i.d. × 250 mm) was used to separate the carbonyl compounds. The column temperature was 40°C, and the flow rate of the mobile phase was 1.0 mL/min. Sample solution (~400 μL) was injected into the HPLC system via the autosampler, and the sample was conveyed by a mixture of acetonitrile and water. The changes in the composition of the mobile phase are shown in Table I.

Calculation of Air Concentrations for Passive Sampling

The reactions of DNPH and carbonyl compounds in the samplers proceed irreversibly. Therefore, the amounts of carbonyl compounds collected by passive sampling reflect the relative air concentrations, indicating a significant correlation with each other. To investigate the relationships between the amounts collected by passive sampling and the air concentrations, we carried out passive and active sampling simultaneously in a temperature-controlled room (20 ± 5°C, *c*.75 m^3). There was no window in the room, and so the resulting indoor carbonyl concentrations were relatively high (e.g. ~114 μg/m^3 for formaldehyde). The sampling periods were varied (2, 4, 6, 8, and 16 h)

TABLE I Experimental conditions for the large-injection-volume method for HPLC analysis of aldehydes

Elution method	*Elution conditions*[a]
I	30% A hold 0.1 min → up to 50% A in a flash, hold 2 min → 80% A (1%/min) hold 6 min → 30% A in a flash
II	40% A hold 0.1 min → up to 50% A in a flash, hold 2 min → 80% A (1%/min) hold 6 min → 40% A in a flash
III	50% A hold 5.0 min → 80% A (1%/min) hold 8 min → 50% A in a flash

[a] Carbonyl concentration, 0.1 μg/mL; A, acetonitrile; B, water.

to obtain the various carbonyl concentrations, and conversion equations for each carbonyl compound were derived from the results.

RESULTS AND DISCUSSION

For passive sampling of carbonyl compounds in the air, increasing the sensitivity of the analysis is crucial. A high sensitivity can be achieved by using highly sensitive detectors, large injection volumes, or both. Highly sensitive detectors are expensive and require longer periods of time, but large injection volumes can be used with widely available devices. Therefore, we adopted the large-injection-volume method.

Factors Affecting the HPLC Retention Times of Carbonyls

The large-injection-volume method generally produces peaks that are broader than those obtained by the normal method, so contracting the peak width is the first objective that must be met. If the injected carbonyl compounds could be held at the front layer of the column, they could be separated with the contraction in peak width. Increases in the retention time of the carbonyl compounds would confirm that the compounds had been held at the front of the column. When we investigated the effect of column temperature (25–50°C), we did not observe any significant increase in the retention times of carbonyls (data not shown). We next investigated the effects of the composition of the mobile phase (Fig. 2). The retention times of formaldehyde and acetaldehyde clearly increased when the acetonitrile composition was decreased, thus indicating that these compounds were concentrated at the front layer of the column. The long retention times we obtained by varying the composition of the mobile phase indicated that this approach would be applicable for the large-injection-volume method.

Dissolubility and Quantitation of Carbonyls by HPLC Analysis

In the large-injection-volume method, differences between the sample solvent and the mobile phase give rise to corrupted peak shapes and variable retention times in HPLC analysis, so the two solvent systems must contain the same components. Furthermore, the composition of the mobile phase can affect the peak shapes. We investigated the variance of peak width at half height (half width) with the acetonitrile proportion in the mobile phase (30–50%) and with the injection volume (10–400 μL; the HPLC conditions are shown in Table I). We found that the half widths did not increase

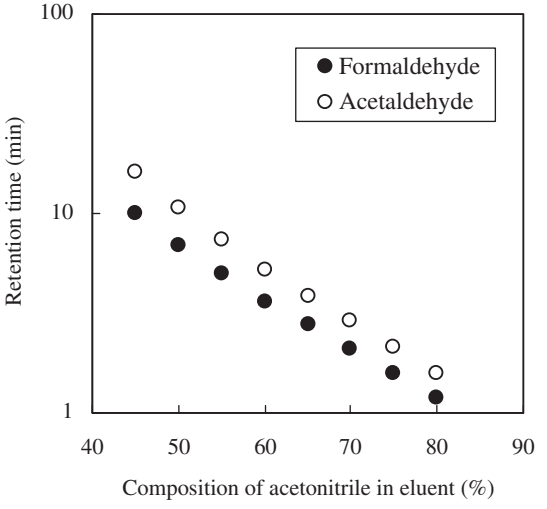

FIGURE 2 Relationship between acetonitrile composition (%) in eluent and retention times of 2,4-DNPH derivatives of carbonyl compounds.

TABLE II Relationship between injection volume and peak half width of carbonyl compounds

Eluent method[a]	*Injection volume* (μL)	*Half width* (min)[b]				
		Formaldehyde	*Acetaldehyde*	*Crotonaldehyde*	*Benzaldehyde*	*o-Tolualdehyde*
I	10	0.14	0.17	0.19	0.20	0.21
	20	0.14	0.17	0.19	0.20	0.21
	50	0.14	0.17	0.19	0.20	0.21
	100	0.14	0.17	0.19	0.20	0.21
	200	0.14	0.17	0.19	0.20	0.21
	400	0.15	0.18	0.19	0.20	0.21
II	10	0.15	0.17	0.20	0.21	0.21
	20	0.15	0.17	0.20	0.20	0.21
	50	0.15	0.17	0.20	0.20	0.21
	100	0.15	0.17	0.20	0.20	0.21
	200	0.16	0.18	0.20	0.20	0.21
	400	0.20	0.20	0.20	0.20	0.21
III	10	0.19	0.22	0.21	0.22	0.21
	20	0.19	0.22	0.21	0.21	0.22
	50	0.19	0.22	0.22	0.21	0.22
	100	0.21	0.23	0.22	0.21	0.22
	200	0.26	0.27	0.23	0.22	0.22
	400	0.41	0.37	0.25	0.22	0.22

[a] See Table I for elution conditions.
[b] Measured at 50% peak height.

with increasing injection volume, whereas the half widths did tend to increase as the proportion of acetonitrile increased (Table II). These results indicated that an initial acetonitrile composition of 30% was optimum (method I, Table I). Under these conditions, the variability in the carbonyl retention times was within 0.12% when the injection volume was varied from 10 to 400 μL (Table III). In addition, the relationship between the injection volume and the corresponding peak area showed

TABLE III Relationship between injection volume and retention times of carbonyl compounds

Injection volume (μL)	*Retention time* (min)				
	Formaldehyde	*Acetaldehyde*	*Crotonaldehyde*	*Benzaldehyde*	*o-Tolualdehyde*
10	12.13	14.79	22.76	27.40	31.65
20	12.11	14.77	22.72	27.37	31.63
50	12.14	14.78	22.75	27.39	31.64
100	12.13	14.78	22.74	27.39	31.64
200	12.15	14.79	22.75	27.40	31.64
400	12.12	14.75	22.72	27.37	31.62
CV	0.12%	0.10%	0.07%	0.05%	0.03%

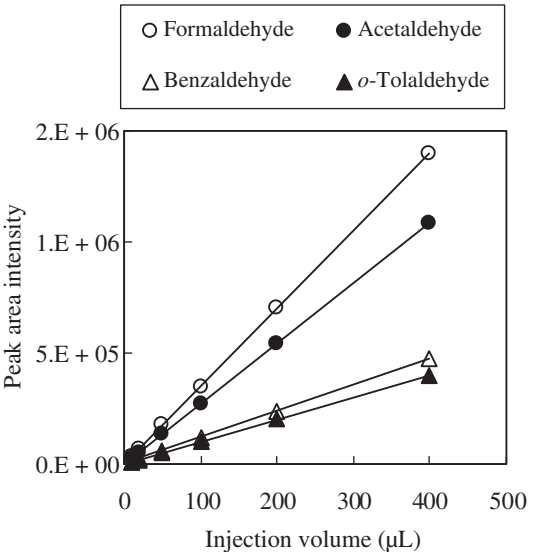

FIGURE 3 Relationship between injection volumes and peak areas of 2,4-DNPH derivatives of carbonyl compounds.

significant linearity ($R^2 = 0.999$–1.000, $p < 0.01$, *t*-test) for all the carbonyl compounds (Fig. 3). Under these conditions, the method's detection limits for carbonyl compounds, which were defined as three times the standard deviation of the peak area determined from repeat injections of a dilute standard solution, ranged from 0.026 (acetone) to 0.152 ng (*o*-tolualdehyde). The dissolubility and the shapes of the carbonyl peaks on the HPLC chromatogram were also satisfactory, although the acrolein and propionaldehyde peaks overlapped (Fig. 4).

Application to the Passive Sampler

To estimate the air concentrations of carbonyl compounds from the amounts collected by the passive sampler, we carried out simultaneous measurements with passive and active samplers in a temperature-controlled room with relatively high air concentrations of carbonyl compounds, and derived conversion equations for each compound. The variability of carbonyl compound concentrations was adjusted by sampling

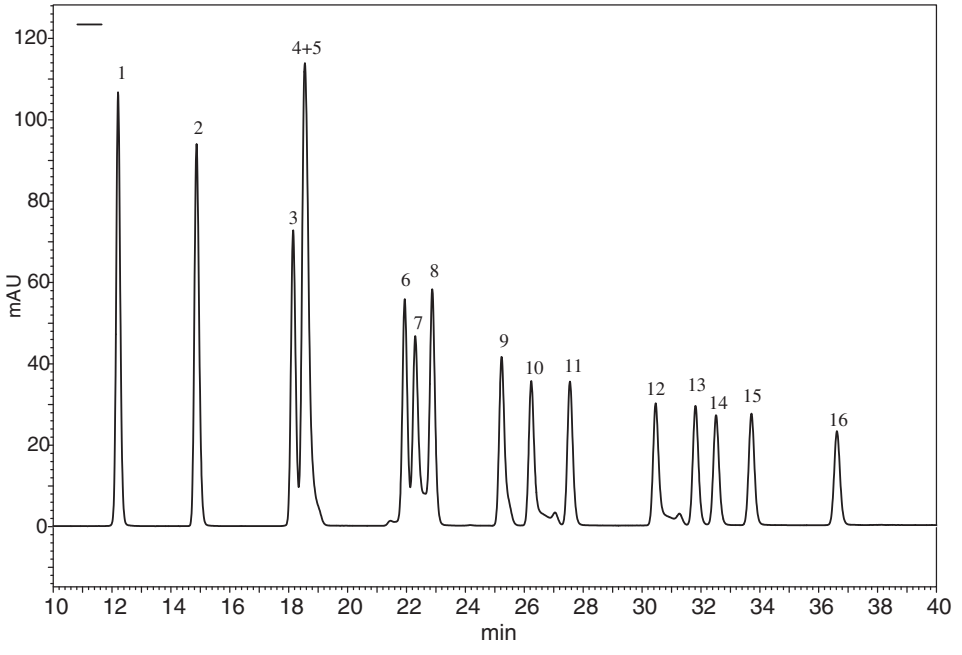

FIGURE 4 HPLC chromatogram of 2,4-DNPH derivatives of each carbonyl compound (0.1 μg/mL). 1, formaldehyde; 2, acetaldehyde; 3, acetone; 4, acrolein; 5, propionaldehyde; 6, *i*-butylaldehyde; 7, *n*-butylaldehyde; 8, crotonaldehyde; 9, *i*-valeraldehyde; 10, *n*-valeraldehyde; 11, benzaldehyde; 12, hexaldehyde; 13, *o*-tolualdehyde; 14, *m*-tolualdehyde; 15, *p*-tolualdehyde; 16, 2,5-dimethylbenzaldehyde. Injection volume, 400 μL.

time (~16 h). Ten carbonyl compounds were collected: formaldehyde, acetaldehyde, acetone, propionaldehyde, *i*- and *n*-butylaldehyde, *i*- and *n*-valeraldehyde, benzaldehyde, and hexaldehyde. Note that unsaturated aldehydes such as acrolein and crotonaldehyde were not determined, because they react with DNPH to form not only one by one product but also one by two or two by three products [31,32]. The amounts of aldehydes collected by passive sampling were linearly correlated with the concentrations measured by active sampling (curves for formaldehyde and acetaldehyde are shown in Fig. 5). The regression plot of y (the amounts from passive sampling, μg) vs. x (air concentrations from active sampling, $\mu g/m^3$) yielded a conversion equation for calculating the air concentrations from the passive sampler data:

$$c = 10^{[\log(y)-b]/a}, \tag{1}$$

where c is the concentration of the carbonyl compound in air ($\mu g/m^3$); y is the amount of the carbonyl collected by the passive sampler (μg); and a and b are constants.

The values of constants a and b and the correlation coefficients for active and passive sampling indicated that the relationships were statistically significant ($p < 0.01$, t-test) for all the carbonyl compounds obtained (Table IV). Here, we do not examine the influence of determining concentrations by humidity, because Levin *et al.* have demonstrated that humidity does not influence the sampling rate of airborne carbonyls using the passive sampler [27]. In addition, the conversion equation was created using the

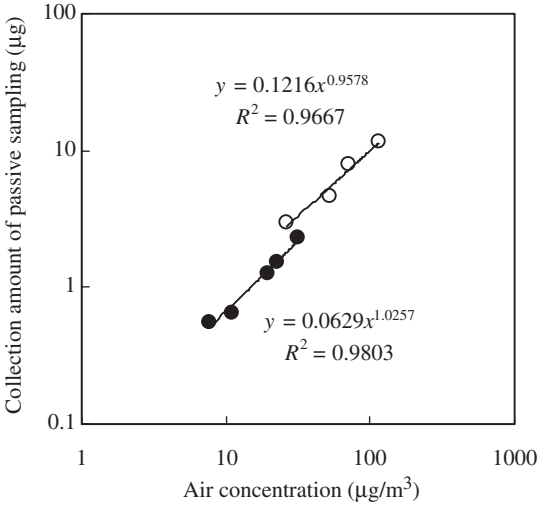

FIGURE 5 Relationship between the amounts of carbonyl compounds collected by passive sampling and the air concentrations of carbonyl compounds determined by active sampling: (○) formaldehyde and (●) acetaldehyde.

TABLE IV Constants for calculation of carbonyl concentrations using Eq. (1)

Compound	*a*	*b*	R^2
Formaldehyde	0.958	−0.915	0.997
Acetaldehyde	1.026	−1.201	0.980
Acetone	0.745	−0.797	0.960
Propionaldehyde	0.943	−1.261	0.991
i-Butylaldehyde	0.842	−1.421	0.991
n-Butylaldehyde	0.754	−1.290	0.967
i-Valeraldehyde	1.295	−1.381	0.972
n-Valeraldehyde	1.021	−1.502	0.963
Benzaldehyde	0.799	−1.230	0.928
Hexaldehyde	0.844	−1.256	0.984

active sampler; here, the ozone scrubber was not connected to the upstream end of the sampler, because the reaction with ozone for the passive sampler remained unclear. That is, the conversion equation could define the carbonyl concentration including the effect of ozone.

To confirm the reliability of passive sampling for carbonyl compounds in air, we surveyed indoor air (three restrooms, a library, and an office), again confirming the accuracy of the method by simultaneously using passive and active samplers. When laboratory blanks ($n = 6$) were analysed by the established method, formaldehyde, acetaldehyde, and acetone were detected at 70, 153, and 53 ng, respectively. The other carbonyl compounds were detected at levels below 10 ng, which suggests that they have little influence on the indoor surveys. From the surveys, nine species of carbonyl compounds were determined by means of both passive and active sampling. The calculated air concentrations were approximately consistent with the concentrations measured by active sampling, whereas the deviations of data between the two

TABLE V Carbonyl concentrations ($\mu g/m^3$) obtained by active and passive sampling in indoor air in restrooms, a library, and an office

Compound	*Restroom (1st)*		*Restroom (2nd)*		*Restroom (3rd)*		*Library*		*Office*	
	Active	*Passive*	*Active*	*Passive*	*Active*	*Passive*	*Active*	*Passive*	*Active*	*Passive*
Formaldehyde	24.9	19.8	11.9	14.0	16.1	16.6	10.1	10.8	8.80	10.2
Acetaldehyde	10.4	9.80	6.17	5.35	6.98	4.59	4.96	6.04	5.78	7.16
Acetone	50.5	56.8	31.4	26.8	83.0	117	5.85	2.59	32.5	31.7
Propionaldehyde	1.05	1.22	0.66	1.02	0.40	0.22	1.23	1.53	0.71	1.17
i-Butylaldehyde	0.60	0.47	0.30	0.45	0.53	0.42	0.10	0.21	0.10	0.22
i-Valeraldehyde	0.35	0.56	0.14	0.32	0.28	0.48	0.07	0.05	0.10	0.22
n-Valeraldehyde	0.79	1.72	0.80	1.48	0.93	1.31	0.57	1.46	0.42	1.72
Benzaldehyde	1.77	0.72	1.06	0.81	0.46	0.67	0.60	0.45	0.80	0.66
Hexaldehyde	1.21	1.12	0.56	0.66	0.63	0.74	2.05	1.42	1.30	0.94

samplings were observed in some carbonyl compounds. This may be caused by the interference of other pollutants, such as ozone, and the extraction. Consequently, by using the large-injection-volume method under suitable HPLC conditions, we were able to use a passive sampler to determine not only formaldehyde and acetaldehyde but also other carbonyl compounds in air. In addition, we were able to estimate the air concentrations of carbonyl compounds collected in the passive sampler by using conversion equations derived from the simultaneous surveys using the active sampler.

It is known that, with active sampling of carbonyl compounds in air, ozone in the sample stream may react with the adsorbed carbonyl compounds [33–38]. This phenomenon must be considered in analysing the accuracy of active sampling. However, it is not clear whether reaction with ozone is a problem for passive samplers. Further research may be needed to improve the reliability of the passive sampling method for determining carbonyl compounds in air.

Acknowledgements

We thank Dr Yoshihiro Suzuki and Dr Yasunori Enomoto, Sibata Scientific Technology Ltd, and Dr Toshiya Sasaki, Waters Co., for supporting this work.

References

[1] V.J. Feron, H.P. Til, F. Devrijer, R.A. Woutersen, F.R. Cassee and P.J. Vanbladeren, *Mutat. Res.*, **259**, 363–385 (1991).
[2] W.P.L. Carter, *Atmos. Environ.*, **29**, 2513–2527 (1995).
[3] D.J. Lary and D.E.J. Shallcross, *J. Geophys. Res.*, **105**, 19771–19778 (2000).
[4] G.C. Morrison and W.W. Nazaroff, *Environ. Sci. Technol.*, **36**, 2185–2192 (2002).
[5] Ministry of Environment (Environment Council), *J. Jpn. Soc. Atmos. Environ.*, **32**, 11–15 (1997).
[6] *Guideline for indoor air pollution*, 2002, Ministry of Health, Labor & Welfare, Japan.
[7] M. Ando, *Bull. Natl. Inst. Health Sci.*, **120**, 6–38 (2002).
[8] *Cabinet Odor for Offensive Odor Control Law*, Ministry of Environment, Japan, 1993, No. 201.
[9] K. Kuwata, M. Uebori and Y. Yamazaki, *J. Chromatogr. Sci.*, **17**, 264–268 (1979).
[10] R.K. Beasley, C.E. Hoffmann, M.L. Rueppel and J.W. Worley, *Anal. Chem.*, **52**, 1110–1114 (1980).
[11] K. Fung and D. Grosjean, *Anal. Chem.*, **53**, 168–171 (1981).
[12] D.C. Lowe, U. Schmidt, D. Ehhalt, C.G.B. Frischkorn and H.W. Nurnberg, *Environ. Sci. Technol.*, **15**, 819–822 (1981).
[13] K. Kuwata, M. Uebori, H. Yamasaki and Y. Kuge, *Anal. Chem.*, **55**, 2013–2016 (1983).
[14] C.M. Druzik, D. Grosjean, A.V. Neste and S.S. Parmar, *Int. J. Environ. Anal. Chem.*, **38**, 495–512 (1990).

[15] J. Zhang, Q. He and P.J. Lioy, *Environ. Sci. Technol.*, **28**, 146–152 (1994).
[16] W. Potter and U. Karst, *Anal. Chem.*, **68**, 3354–3358 (1996).
[17] E. Grosjean and D. Grosjean, *Environ. Sci. Technol.*, **30**, 859–863 (1996).
[18] D. Grosjean, *Environ. Sci. Technol.*, **16**, 254–262 (1982).
[19] D. Grosjean, *Environ. Sci. Technol.*, **25**, 710–715 (1991).
[20] E. Grosjean, D. Grosjean, M.P. Fraser and G.R. Cass, *Environ. Sci. Technol.*, **30**, 2687–2703 (1996).
[21] E.L. Viskari, M. Vartiainen and P. Pasanen, *Atmos. Environ.*, **34**, 917–923 (2000).
[22] D.W.M. Sin, Y.C. Wong and P.K.K. Louie, *Atmos. Environ.*, **35**, 5961–5969 (2001).
[23] K.F. Ho, P.K.K. Louie and S.C. Zou, *Atmos. Environ.*, **36**, 1259–1265 (2002).
[24] S.M. Correa, E.M. Martins and G. Arbilla, *Atmos. Environ.*, **37**, 23–29 (2003).
[25] E.B. Bakeas, D.I. Argyris and P.A. Siskos, *Chemosphere*, **52**, 805–813 (2003).
[26] A. Baez, H. Padilla, R. Garcia, M.C. Torres, I. Rosas and R. Belmont, *Sci. Total Environ.*, **302**, 211–226 (2003).
[27] J.O. Levin, R. Lindahl and K. Andersson, *Environ. Sci. Technol.*, **20**, 1273–1276 (1986).
[28] J.D. Mulik, R.G. Lewis and W.A. McClenny, *Anal. Chem.*, **61**, 187–189 (1989).
[29] R.W. Gillett, H. Kreibich and G.P. Ayers, *Environ. Sci. Technol.*, **34**, 2051–2056 (2000).
[30] K. Sakai, D. Norback, Y. Mi, E. Shibata, M. Kamijima, T. Yamada and Y. Takeuchi, *Environ. Res.*, **94**, 75–85 (2004).
[31] R. Schulte-Ladbeck, R. Lindahl, J.-O. Levin and U. Karst, *J. Environ. Monit.*, **3**, 306–310 (2001).
[32] L.-J.S. Liu, R.L. Dills, M. Paulsen and D.A. Kalman, *Environ. Sci. Technol.*, **35**, 2301–2308, (2001).
[33] R.R. Arnts and S.B. Tejada, *Environ. Sci. Technol.*, **23**, 1428–1430, (1989).
[34] E. Grosjean, J.B. de Andrade and D. Grosjean, *Environ. Sci. Technol.*, **30**, 975–983, (1996).
[35] E. Grosjean and D. Grosjean, *Environ. Sci. Technol.*, **31**, 2421–2427, (1997)..
[36] T.E. Kleindienst, E.W. Corse, F.T. Blanchard and W.A. Lonneman, *Environ. Sci. Technol.*, **32**, 124–130, (1998).
[37] M. Duane, B. Poma, D. Rembges, C. Astrga and B.R. Larsen, *Atmos. Environ.*, **36**, 3867–3879, (2002).
[38] M. Possanzini, V.D. Palo and A. Cecinato, *Atmos. Environ.*, **37**, 1309–1316, (2003).