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A quartz crystal microbalance sensor for the detection of formic acid vapors

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Abstract A new quartz crystal microbalance sensor is developed to determine formic acid at low concentrations. Four previously selected polymers with acid–base characteristics were tested as possible coatings. Polyoxyethylene bis [amine] presented the best results. The sensor is rapid, sensitive [0.67 Hz/(mg/m^3)], and reversible at low concentrations. The detection limit for formic acid (7.2 mg/m^3) is comparable with the short term exposure limit and the threshold limit values. It presents a fast mechanical response to pressure changes, so that it can be quickly used in different environments and situations. The sensor also shows a good stability in a temperature range typical of work atmospheres (16–36 °C). It has a wide linear range (7.2–911.2 mg/m^3) and a long useful time. It is also applicable to other low molecular mass carboxylic acids such as acetic acid.

1 Introduction

Since Sauerbrey [1] described a linear relationship between the oscillating-frequency shift and the mass of a substance adsorbed onto the surface of a piezoelectric quartz crystal vibrating in a thickness shear mode (TSM), many hazardous gases and vapors have been resolved [2–5] based upon traditional piezoelectric TSM acoustic-wave vapor sensors, usually coated with liquid or rubbery solid polymers. Responses of these sensors vary in direct proportion to the extent of vapor sorption, which is typically rapid, reversible, and a linear function of vapor concentration. Nowadays some studies are aimed at finding several partially selective coatings that present a partial response to an amount of different analytes and it is hoped to avoid the problems of selectivity with statistical techniques [6]. However, there are applications in which high selectivity is not a critical problem but only group selectivity is required or even none at all, because the requirement is to determine the concentration of a known agent in the absence of interfering substances. Under these circumstances, sensitivity, reversibility, and reproducibility become the predominant requirements [7].

Some efforts have been made [8–12] to develop TSM sensors to detect carboxylic acids such as acetic or formic acids in air. The American Conference of Governmental Industrial Hygienists (ACGIH) has assigned formic acid a threshold limit value (TLV) of 9.4 mg/m^3 as a time-weighted average (TWA) concentration for a normal 8 h working day and a 40 h working week and a short-term exposure limit (STEL) of 19 mg/m^3 for periods not to exceed 15 min, not to be repeated more than four times a day and separated by intervals of at least 60 min. For acetic acid, the TLV is 25 mg/m^3 and the STEL is 37 mg/m^3 [13–15].

In the present paper, a TSM acoustic-sensor has been developed for sensing formic acid with a low detection limit and good sensitivity at low concentrations. Four coatings with acid–base characteristics have been studied. Polyoxyethylene bis (amine) presented the best results. Other carboxylic acid vapors such as acetic acid can be detected as it presents a good group selectivity.

2 Experimental

2.1 Instrumentation

The piezoelectric quartz crystal, vibrating in the TSM, was an AT-cut HC-6/U with gold electrodes on each side (INYSA, Spain), with a fundamental resonance frequency of 9 MHz. The diameter of the crystal was about 11 mm and that of the gold electrodes about 5 mm. The electronic circuitry was designed in accordance with others used previously [8–10]. The frequency change of the oscillating crystal was monitored using a digital frequency counter (BREMI INSTRUMENTS, BRI 9130).

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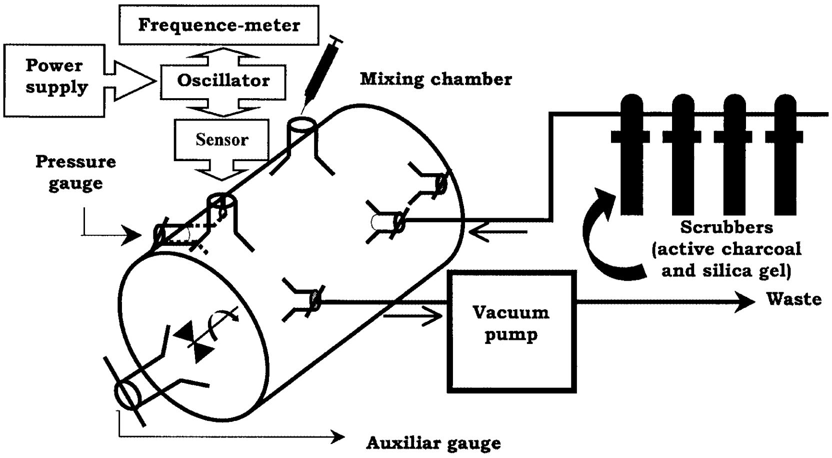

Fig. 1 A diagram of the vapor generator system

2.2 Reagents

All reagents were analytical grade and were used without further purification. The polymers used as coatings were methoxypolyoxyethylene amine (MPOEA), bis (polyoxyethylene bis [amine]) (bPOEbA), polyoxyethylene bis (amine) (POEbA) and polyoxyethylene bis (3-amino-2-hydroxypropyl) (POEb(3A2H)) and they were all obtained from Sigma (St. Louis, Mo., USA). The solvents used were doubly distilled water and acetone, which was from Merck (Darmstadt, Germany). The rest of the compounds (analytes and interferents) were all from Merck (Darmstadt, Germany).

Air was drawn from the laboratory and it was purified with activated charcoal and dried with silica gel while being introduced in the mixing chamber.

2.3 Mode of coating

Several solutions were prepared with the appropriate solvent for each coating. Doubly distilled water was used as solvent for bPOEbA and MPOEA, and acetone was used to dissolve POEbA and POEb(3A2H). The coating process consisted of dropping the required amount of solution onto each surface in order to obtain the desired coating frequency shift. Vaporization of the solvent was completed in an oven at 75 °C for 3 h. All the crystals were stored in a desiccator with silica gel. The amount of coating is given as frequency shift and it is measured in hertz.

2.4 Sampling and procedure for obtaining the signal

The system used for sampling is represented in Fig. 1; it was conveniently thermostated within 25 ± 0.5 °C. The procedure for generating the vapor mixture was essentially static and it was as follows:

In a first step, the previous base frequency data are collected. In step 2, a vacuum is generated for 1 min ($\Delta p = -100.7$ kPa). In step 3, the required amount of analyte is injected with a microsyringe and time is allowed for a complete vaporization (1 min). In step 4 the system is filled with clean dried air and, finally, in step 5, frequency data for response are collected for 5 min.

The signal is the difference between the frequency data obtained in step 5 and the initial frequency data obtained in the first step.

3 Results and discussion

3.1 Vapor generation

The procedure for vapor generation presented in this work is a modification of other procedures found in the literature [8–10]. In this case, only the sensor crystal is into the mixing chamber to reduce typical sorption problems in static methods for vapor generation. The previous frequency data were collected for 30 s to ensure that the signal was stable. Vacuum generation ($\Delta p = -100.7$ kPa) was observed on the pressure gauge to be completed after 1 min. The pressure gauge was not sensitive enough to detect an increase of the inner pressure when the vaporization of the analyte was complete. An alternative method for controlling the time needed to have a complete vaporization was filling up with clean dried air at different vaporization times. The analyte–air mixture was removed with a gas syringe from the mixing chamber and injected into a gas chromatograph. Several problems in reproducibility were found in this process, so that it was considered necessary to fall back on an uncoated crystal as piezoelectric crystals are very sensitive to pressure changes. The frequency was stabilized 40 s after the injection of the less volatile analytes tested. This time was reduced to less than 10 s in the case of very volatile analytes. In this way, the time for step 3 was considered to be 1 min. Filling up with clean dried air was observed on the pressure gauge to be completed after 50 s. 1 min was established for step 4. The time for collection of frequency data was established in order to carry out an analysis and a cleaning of the system for it to be ready for a new analysis in 15 min; just the same time as the period not to be exceeded at the STEL concentration; hence, that time was set at 5 min. The signal was the difference between the frequency obtained after these 5 min and the initial frequency.

3.2 Preliminary tests of frequency-shift responses

Several piezoelectric crystals were coated with previously selected polymers, MPOEA, POEb(3A2H), bPOEbA, and POEbA, and were placed in the presence of a number of different organic vapors, such as aliphatic carboxylic acids, alcohols, ketones, etc. Formic acid vapor was one of these vapors, and so was acetic acid, as representatives of low molecular mass carboxylic acids. We tried to ensure that the amounts of coating were similar, so that the coated

Table 1 Preliminary results for frequency-shift responses of several piezoelectric crystals coated with previously selected polymers and exposed to a number of different organic vapors. Responses are the average of three measurements and they are expressed in Hz. The standard deviations appear in parentheses

Vapor	Conc. (mg/m^3)	Coating (amount in Hz)			
		MPOEA (–7890)	POEb(3A2H) (–6577)	bPOEbA (–8915)	POEbA (–4782)
Acetone	14751	–17 (2)	–25 (2)	–6 (2)	–7 (2)
Ethyl methyl ketone	15040	–63 (2)	–22 (5)	–25 (1)	–23 (1)
Acetaldehyde	14629	–27 (2)	–41 (5)	–14 (2)	–32 (2)
Propionaldehyde	15048	–22 (4)	–42 (2)	–14 (2)	–21 (1)
Ethyl acetate	16813	–35 (3)	–37 (1)	–20 (1)	–44 (3)
n-Butyl acetate	16480	–45 (1)	–50 (3)	–19 (4)	–43 (5)
Ethanol	14740	–18 (1)	–98 (3)	–38 (4)	–96 (4)
Methanol	14779	–49 (5)	–73 (4)	–37 (5)	–67 (3)
Acetic acid	1959	–171 (6)	–219 (11)	–188 (9)	–243 (11)
Formic acid	2278	–472 (10)	–670 (37)	–94 (12)	–1109 (12)
Water	1867	–36 (2)	–70 (11)	–23 (6)	–40 (5)

crystal with the best response to formic acid was chosen in order to improve its possible real applicability. The results are given in Table 1. All the selected coatings presented good responses to formic and acetic acid, except bPOEbA, which apparently presented some problems of irreversibility when testing acetic and formic acid, as the base frequency values could not be re-established after cleaning. Responses of the other three coatings were clearly higher for carboxylic acids than for the other functional groups initially tested, which was considered relevant for group selectivity.

POEbA was the polymer that undoubtedly presented the best sensitivity to a carboxylic acid such as formic acid or acetic acid as its signal was about the double that presented by the other two polymers, MPEA and POEb(3A2H). That was why it was chosen as the best candidate for improving its possible real applicability.

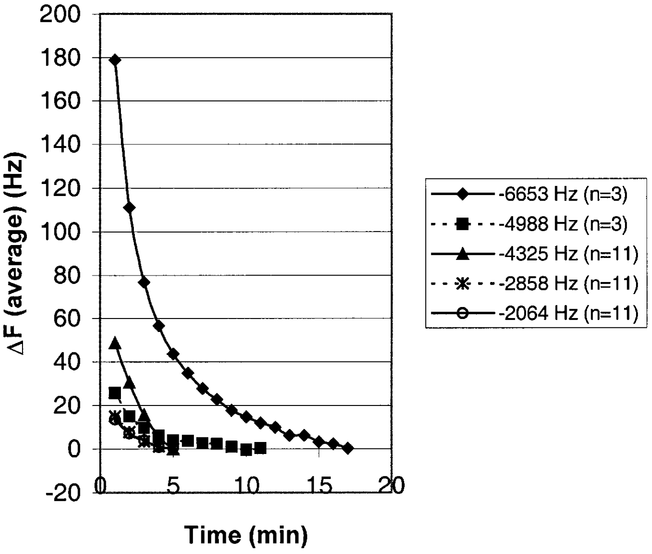

Fig. 2 Differences of frequency with respect to the initial frequency as a function of time after filling up with air for several coating amounts

3.3 Mechanical influence of the coating

As the polymer (POEbA) modifies the mechanical properties of the vibrating crystal, the influence of the amount of coating polymer was studied. The initial frequency was recorded, vacuum was generated ($\Delta p = -100.7$ kPa) and the apparatus was filled with clean dried air until the initial pressure was re-established The frequency values were recorded at different times and compared with the initial frequency. An amount of coating polymer was considered appropriate if the initial base frequency coincided with the final frequency just in the prearranged time to do an analysis. Such marked changes in pressure are not very common, so that this conditions very unfavorable, which ensures that the coated crystal will be quickly adapted to more usual pressure changes.

Several amounts of coating were tested. These corresponded to –6653, –4988, –4325, –2858, and –2064 Hz. The results of these differences of frequency are presented in Fig. 2.

When the crystal coating corresponded to –6653 and –4988 Hz, the analysis required more than 5 min, so that these amounts of coating were rejected as having a too slow mechanical response to pressure changes. When the crystal coating corresponded to –4325 Hz, it reached the initial frequency within 5 min, which was considered quick enough. When smaller amounts of coating were tested, more rapid responses to pressure changes were obtained, so that they could be quickly used in different environments and situations.

It should be noted that the responses of the last three amounts of coating indicated a good repeatability to clean and dry air in this 5 min.

3.4 Sensitivities and detection limits

Calibration graphs were obtained for the three coating amounts for formic acid.

A significant influence of the mass of the coating on the sensitivities was found for a carboxylic acid such as

Table 2 Calibrations obtained for a carboxylic acid (formic or acetic, as indicated) with a crystal coated with different amounts of POEbA (ΔF is measured in Hz and C is measured in mg/m^3)

Acid	Coating amount (Hz)	Range studied (mg/m^3)	Curve equation	R^2
Formic	–2064	22.8–592.3	$\Delta F = 0.22\,°C + 1.70$	0.9986
	–2858	17.8–592.3	$\Delta F = 0.23\,°C + 0.56$	0.9972
	–4325	7.2–911.2	$\Delta F = 0.67\,°C - 0.59$	0.9988
Acetic	–4325	18.6–911.2	$\Delta F = 0.36\,°C - 2.47$	0.9963

formic acid, so that the optimum amount of POEbA to be applied to the sensor corresponded to –4325 Hz. Results are shown in Table 2.

An important influence of the mass of the coating on the detection limit for formic acid was also found, with the best result being for the same coating amount as for the sensitivity, i.e. for –4325 Hz. The detection limit (7.2 mg/m^3) is of the order of magnitude of the STEL and TLV. The detection limit was taken as the vapor concentration in the mixture, giving a frequency shift equal to that of the blank (clean dried air) plus three times its standard deviation.

A calibration graph was also obtained for acetic acid with a –4325 Hz POEbA coating; as expected, a lower sensitivity to acetic acid and a higher detection limit (18.6 mg/m^3) were found, which is attributable to its lower acid strength, so that less sorption takes place. Anyhow, this amount of coating shows a very good behavior for carboxylic acids, such as formic acid and acetic acid.

3.5 Repeatability and stability

The sensor coated with POEbA to –4325 Hz was alternatively exposed six times to the presence of formic acid vapor at two different concentrations (55.0 and 30.0 mg/m^3). The frequency-shift response data of the sensor are listed in Table 3. The relative standard deviations (RSDs) were 4.5% and 6.6% for 55.0 and 30.0 mg/m^3, respectively, indicating that the sensor shows a good repeatability for the detection of a carboxylic acid such as formic acid at low concentrations.

In order to establish the stability of the sensor device, 11 uninterrupted analyses were carried out for a total time of 165 min when the sensor was continuously exposed to formic acid at a concentration of 55 mg/m^3. The average signal was 35.9 Hz, with a standard deviation of 1.4 and an RSD of 3.8%, indicating that the sensor possesses a good stability.

Table 3 Repeatability of the sensor coated with POEbA corresponding to –4325 Hz. The sensor was alternately exposed to formic acid at concentrations given in the left and right columns

No.	Frequency-shift response (ΔF, Hz)	
	55.0 mg/m^3 formic acid	30.0 mg/m^3 formic acid
1	36	17
2	34	17
3	35	19
4	34	18
5	37	18
6	38	20
A.V.	35.7	18.2
S.D.	1.6	1.2

3.6 Reversibility of the sorption process

Initial base frequencies were compared with that obtained after the cleaning process, when different concentrations of carboxylic acid were injected, to study the reversibility of the sorption process. The difference of these data ($\Delta F_{\text{rev.}} = F_{\text{clean.}} - F_{\text{base}}$) gives an idea of the retention of acid on the surface of the coated crystal as a function of concentration. Figures 3 a and 3 b, respectively, show the results obtained for formic acid and acetic acid.

A slight retention process occurs when analyzing formic acid ($\Delta F_{\text{rev.}} = -0.08\,°C + 5.58$, $R^2 = 0.9941$), which suggests that, although the sorption process is mainly physical, there is a slight contribution of chemisorption that would limit the number of short-dated analyses that could be made if the concentration of formic acid were higher than 66.6 mg/m^3. This is the concentration for which $\Delta F_{\text{rev.}} = 0$ Hz in the calibration graph proposed above; when this quantity was tested, no retention signal was obtained.

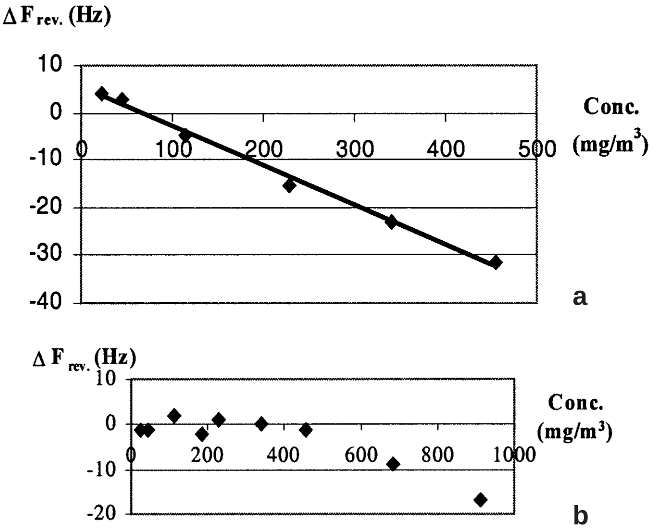

Fig. 3 Differences of base frequency from that obtained after the cleaning process at different concentrations for low molecular mass carboxylic acids such as (**a**) formic acid and (**b**) acetic acid

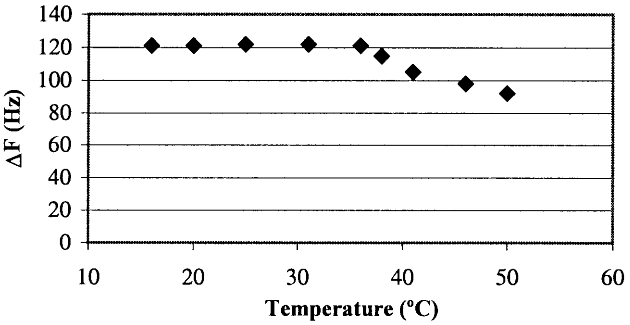

Fig. 4 Influence of temperature when injecting 182.2 mg/m^3 of formic acid vapor

As acetic acid is a weaker carboxylic acid than formic acid, the chemisorption process is not detectable even at 455.6 mg/m^3.

The sorption effects could be based on the following fundamental mechanisms in order of interaction energy: (I) polar interactions (dipole–dipole); (II) H bonding between the carboxylic acid group of the analyte and the ether group of the coating polymer; (III) Lewis acid–base interaction between the amine group of the coating polymer and the carboxylic acid group of the analyte that would be responsible for the irreversibility. This interaction would mainly explain why formic acid presents a chemisorption that is detectable at lower concentrations than acetic acid. It is difficult to propose only one type of interaction since the coating functional groups have more than one way to interact with the analyte molecule; for example, acidic and basic groups are also polar, so that a dipole–dipole interaction is also possible.

3.7 Effect of temperature

The effect of temperature in the range 16–50 °C on the quartz crystal coated to give –4325 Hz was studied when the crystal was exposed to a carboxylic acid such as formic acid vapor (182.2 mg/m^3). Results are shown in Fig. 4.

There is a range (16–36 °C) in which the sensor shows a very good stability in the frequency-shift response. For higher temperatures, the frequency-shift response diminished (–2 Hz/ °C), showing that the sorption of formic acid by POEbA decreases with increasing temperature.

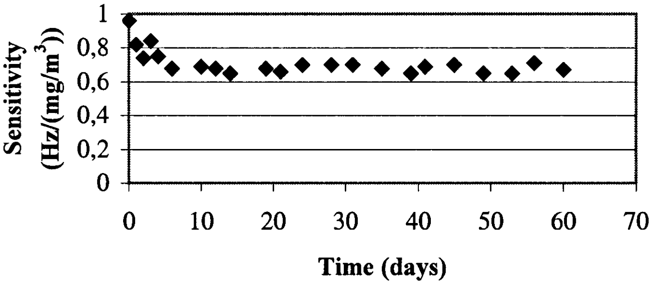

Fig. 5 Sensitivity versus time upon exposure to formic acid vapor for the TSM sensor coated with POEbA corresponding to –4325 Hz

3.8 Useful lifetime

The evolution with time of the sensitivity of the frequency-shift response of the TSM sensor when exposed to the vapor of a carboxylic acid such as formic acid has been studied in detail for 2 months. Figure 5 shows that there was a fluctuation over the first 4 days but the sensitivity did not vary dramatically over the rest of the time period studied. After these first 4 days, the RSD of the sensitivity was 3.0% so that the sensor shows a useful lifetime of at least 2 months.

3.9 Atmospheres for application of the sensor

A selective response of a unique coated piezoelectric crystal to an analyte is not a very realistic position, but a single analyte may be detected in the presence of other species with different functional groups.

In this way, a sensor to detect formic acid is proposed, but any carboxylic acid will be a serious interferent; for example, with a sensitivity that is about half that for formic acid, acetic acid can also be detected with the same sensor.

Assuming this fact, studies of the kind of atmosphere in which the sensor could be applied were carried out. Table 4 illustrates the results obtained supposing that a compound could be considered as an interferent if its concentration is higher than that indicated in the table.

The concentrations appearing in the table were taken as the vapor concentration in the mixture, giving a frequency shift equal to that of the blank (clean dried air) plus three times its standard deviation.

Table 4 Studies of the kind of atmosphere in which the sensor could be applied: a compound could be considered as an interferent if its concentration is higher than that indicated in the table

Compound	Concentration (mg/m^3)
Acetone	5468
Ethyl methyl ketone	3008
Propionaldehyde	219
Acetaldehyde	298
Ethyl acetate	6834
n-Butyl acetate	2077
Methanol	1089
Ethanol	929
2-Propanol	809
Water	69
1,4-Dioxane	1049
Toluene	4014
Chloroform	4036
Dichloromethane	9755
Dichloroethane	1875
Fluorobenzene	5729
Chlorobenzene	1162
Bromobenzene	518
n-Heptane	Sat.
Cyclohexane	Sat.

4 Conclusions

A new sensor for formic acid is proposed. The sensor is rapid, sensitive, and reversible at low concentrations. It shows a fast mechanical response to pressure changes. The detection limit is only slightly lower than the TLV. This could be a limitation, considering that in practical applications detection limits achieved in the laboratory frequently cannot be obtained. Making the mixture impinge dynamically on the coated crystal may possibly enhance the detection limit. It shows a good stability in a temperature range typical for working atmospheres.

It is also applicable to other low molecular mass carboxylic acids such as acetic acid, as it presents a good group selectivity.

In the future, the sensor developed here could be integrated as part of a sensor array.

References

1. Sauerbrey G (1959) Z Phys 155:206
2. Suleiman AA, Guilbault GG (1994) Stud Environ Sci 59: 273–303
3. Alder JF, McCallum JJ (1983) Analyst 108:1169
4. McCallum JJ (1989) Analyst 114:1173
5. Schumacher R (1990) Angew Chem 4:329
6. Strike DJ, Meijerink, MGH, Koudelka-Hep M, (1999) 364: 499–505
7. Milanko OS, Milinkovic SA, Rajakovic LV (1992) Anal Chim Acta 269:289–300
8. Muñoz Leyva JA, Hidalgo Hidalgo de Cisneros JL, García G, Barreda D (1993) Talanta 40 (11):1725
9. Muñoz Leyva JA, Hidalgo Hidalgo de Cisneros JL, García G, Barreda D, Fraidías Becerra AJ (1993) Analyst 118:175
10. Muñoz Leyva JA, Hidalgo Hidalgo de Cisneros JL, García G, Barreda D, Fraidías Becerra AJ (1994) Talanta 41:159
11. Cao Z, Cao D, Lei Z –G, Lin H-G, Yu R-Q (1997) Talanta 44:1413
12. Xiang J-N, Cao Z, Yin X, Wang K-M, Lin H-G, Yu R-Q (1999) Anal Chim Acta 384:37–44
13. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, National Institute for Occupational Safety and Health (1992) Recommendations for occupational safety and health: Compendium of policy documents and statements. DHHS (NIOSH) Publication No. 92–100, Cincinnati, Ohio
14. American Conference of Governmental Industrial Hygienists (1991) Documentation of the threshold limit values and biological exposure indices, 6th edn. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio
15. American Conference of Governmental Industrial Hygienists (1994) 1994–1995 Threshold limit values for chemical substances and physical agents and biological exposure indices. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio