

HEALTH RISK ASSESSMENT RELATED TO HYDROGEN PEROXIDE PRESENCE IN THE WORKPLACE ATMOSPHERE – ANALYTICAL METHODS EVALUATION FOR AN INNOVATIVE MONITORING PROTOCOL

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Abstract

Objectives: Hydrogen peroxide (HP) accounts for 15% of the total global chemical revenue. According to the National Institute of Occupational Safety and Health, the HP concentration immediately dangerous to human life or health is 75 ppm. Operators exposed to HP should pay attention when choosing the monitoring technique that should be specific and sensitive enough to discriminate the exposure levels from background concentrations. In order to assess the long- and short-term exposure to HP in disinfection processes, the authors compared 6 industrial hygiene monitoring methods to evaluate their efficiency in measuring airborne HP concentrations. **Material and Methods:** Airborne HP concentrations were evaluated using an on-fiber triphenylphosphine solid-phase microextraction method, and they were compared with those obtained using a 13-mm Swinnex titanium oxysulfate filter holder and 4 portable direct-reading electrochemical sensors. A survey carried out in wood pulp bleaching, food and beverage disinfection processing, and in a hospital department to reduce the risk of spreading nosocomial infections, was performed during routine operations to assess the risk of HP occupational exposure. **Results:** Through the generation of HP gaseous dynamic atmospheres (0.1–85 ppm), the authors evaluated the consistency of the results obtained using the 6 methods described. The monitoring campaigns showed that the increase in HP could be

Received: June 27, 2019. Accepted: October 30, 2019.

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relatively high (until 67 ppm) in food and beverage processing. **Conclusions:** In the authors' opinion, the current 8-h time-weighted average limits of 1 ppm for HP do not reflect the actual risk; a short-term exposure limit would, therefore, provide a much better protection. *Int J Occup Med Environ Health.* 2020;33(2):137–50

Key words:

environmental monitoring, occupational medicine, hydrogen peroxide, exposure scenario, airborne exposure, electrochemical sensor

INTRODUCTION

The global market for hydrogen peroxide (HP, CAS No. 7722-84-1) is forecast to reach 5.7 million metric tons by 2022. Asia-Pacific constitutes the largest and fastest growing market worldwide. Hydrogen peroxide accounts for 15% of the total global chemical revenue [1]. The main use of HP in the world is for bleaching pulp. Other uses include chemicals manufacture and HP as an intermediate in the synthesis of chemicals, in the bleaching of textiles, wastewater and waste gas treatment, disinfection, and beverage packing.

The American Conference of Governmental Industrial Hygienists (ACGIH) has indicated that HP is a confirmed animal carcinogen with unknown relevance to human carcinogenicity. Zienolddiny et al. [2] have found that different dilutions of a 30% solution of HP, when added to cell culture mediums, display mutagenic effects, producing reactive oxygen species that could result in direct DNA and protein damage. According to the National Institute of Occupational Safety and Health (NIOSH), the HP concentration immediately dangerous to life and health (IDLH) is 75 ppm.

Currently, there are substantial differences among the guidelines concerning HP occupational exposure provided by various associations, not only in terms of the parts per million limits but also regarding values to be assessed [3]. For example, Deutsche Forschungsgemeinschaft (DFG) proposes recommended exposure limits as an 8-h time-weighted average (TWA) (0.5 ppm) and a short-term exposure limit (STEL) (0.5 ppm), which are significantly lower than the workplace exposure limits indicated by Finland's health and safety executives (1 ppm for TWA and 3 ppm for 15-min STEL). In contrast, the Occupational Safety and Health Administration

(OSHA), NIOSH and ACGIH have established a permissible exposure limit, a recommended exposure limit and a threshold limit value of 1.0 ppm, calculated as an 8-h TWA, and do not indicate HP occupational exposure limits in terms of STEL. The European Union (EU) has proposed an adverse effect level for inhalation exposure equal to 0.9 ppm for acute, medium- and long-term exposure, based on the no-adverse-effect level being observed in a 90-day inhalation rat study [4]. The EU Regulation concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) has set the values of the derived no-effect level (DNEL) for HP at 1.4 mg/m³ and 3 mg/m³ for long-term and acute short-term exposures, respectively [5].

To date, there have been few proposed analytical methods applied in the field of industrial hygiene. These involve the sampling method using titanium tetrachloride, potassium dioxalatoxotitanat(IV), titanium oxysulfate hydrate (TiOSO₄), and triphenylphosphine (TPP) [6–12] as reagents, whether on filters or impingers, followed by colorimetric spectroscopy, pulse polarography or liquid chromatography. Other analytical methods suitable for determining airborne HP concentrations have been proposed in the environmental field, including UV photolysis [13], chemiluminescence [14,15], Fourier transform infrared spectroscopy (FTIR) [16], tunable diode laser absorption spectrometry (TDLAS) [17], and fluorescence spectrometry, with and without chromatographic separation [12,18–20]. Unfortunately, the latter 6 methods require trained operators and rather expensive and complex equipment, in order to be used for analytical purposes, even though they are characterized by low detection limits. In this scenario, the direct determination of HP concentrations for industri-

al hygiene measurements, without preconcentration steps, appears to be remarkable. There is a significant demand for compact instruments that can provide real-time exposure data on-site and require minimum time for preparation and maintenance. Electrochemical sensors for airborne HP detection are small and convenient real-time portable instruments which have recently enjoyed much interest from various authors [21,22]. In 2015, the total opportunity cost for HP measurement devices was USD 28 mln in Europe, projected to expand at a compound annual growth rate (CAGR) of 6.0% in 2016–2024. By the end of 2024, it is likely to reach USD 42.7 mln [23].

The aim of this work is to assess the long- and short-term exposure to airborne HP by comparing 6 analytical methods. This paper describes the evaluation and validation protocol used for assessing the HP occupational exposure levels in food and beverage processing, wood pulp bleaching, and hospital high-level disinfection, during high-risk operations, in line with the exposure scenarios reported in literature [4]. Thus, a new solid-phase microextraction (SPME)/fast gas chromatography (GC)-mass spectrometry (MS) HP detection method has been developed and compared with 4 electrochemical sensors and a modified TiOSO₄ spectrophotometric monitoring to detect overexposure to HP.

MATERIAL AND METHODS

Measurement devices

For the diffusive analytical technique, a Fast Fit Fiber Assemblies (FFA)-SPME 30 µm polydimethylsiloxane fiber (Cat. No. FFA57289-U, Supelco, Bellefonte, USA) was doped for 120 s in the headspace of a 10 ml vial, preheated at 90°C for 20 min and containing 100 mg of TPP (CAS No. 603-35-0, Cat. No. T84409, Sigma-Aldrich, Saint Louis, USA). From the reaction between HP and TPP, triphenylphosphine oxide (TPPO, CAS No. 791-28-6, Cat. No. T84603, Sigma-Aldrich, Saint Louis, USA) was obtained [24,25]. Personal sampling was performed by rapid FFA-SPME [26] (60 s) and by TWA-FFA-SPME [27] (8 h) through a diffusive sam-

pling fiber holder (Supelco, Bellefonte, USA). After sampling, HP was analyzed with fast GC/MS with a Shimadzu GC 2010-MS QP 2010 series (Shimadzu, Kyoto, Japan), operating in the electron ionization (EI) mode, full-scan, using the base peak from the 70 eV EI spectra as the quantitation ion, as follows: TPP (retention time, RT, 4.04 min), m/z 262 and TPPO (RT 4.67 min), m/z 277. The initial oven column temperature for the MEGA-5 MS column (10 m × 0.10 mm × 0.1 µm film thickness, MEGA, Legnano, Italy) was set to 70°C for 0.3 min, and then increased at 50°C/min to 300°C (total run time: 4.90 min). Helium (99.999%) at a flow rate of 1.10 ml/min was used as carrier gas. For desorbing the analytes, the SPME fiber was introduced into the GC injector port and maintained at 280°C for 2 min. Full automation of the procedure was achieved using a new Flex GC autosampler (EST Analytical, Fairfield, USA), equipped with a 45-position Multi Fiber Exchange. The cross reactivity to peracetic acid was avoided through an assembled cassette with a quartz filter impregnated with an ethanol/water 2,2'-azino-bis(3-ethyl-benzothiazoline)-6-sulfonate (ABTS, CAS No. 30931-67-0, Cat. No. 10102946001, Sigma-Aldrich, Saint Louis, USA) solution [28] and connected to FFA-SPME [26].

For active sampling, the method proposed by Hecht et al. [6] was used with some modifications. An air flow ranging 0.1–1.0 l/min was applied to a mini-sampler open-face 13 mm Swinnex holder (Cat. No. 225-6201, Eighty Four, SKC) assembled on a 13-mm quartz filter (Cat. No. A080A013A, Advantec MFS, Inc., Dublin, CA, USA) previously soaked with 100 µl of 50 mg/ml 0.9 M H₂SO₄ TiOSO₄ (CAS No. 123334-00-9, Cat. No. 463914, Sigma-Aldrich, Saint Louis, USA), and then dried for 1 h in an oven at 60°C. Moreover, to enable the positioning of the sampler inlets within the proximity of the operator's nose and mouth, the authors used a face-level sampling headset (Cat. No. 225-6200, SKC, Eighty Four, USA). The GilAir Plus personal sampling pumps were supplied by Sensydine (St. Petersburg, USA). After sampling,

Table 1. The technical data of the direct reading of electrochemical instruments and GC/MS laboratory analytical methods in the study on hydrogen peroxide monitoring

Instrument	Sampling mode	Measuring range [ppm]	Resolution [ppm]	Detection system
ATI Series C16 PortaSens II (Analytical Technology Inc, Colleagueville, USA)	active	0–200	0.1	electrochemical
Interscan 4000 Series Compact (Interscan Corporation, Simi Valley, USA)	active	0–199.9	0.1	electrochemical voltammetric sensor
SafeCide portable monitoring system (ChemDAQ, Pittsburgh, USA)	passive	0–20	0.1	electrochemical
Dräger X-am 5100 (Drägerwerk AG & Co. KGaA, Lübeck, Germany)	passive	0–20	0.1	electrochemical
Swinnex titanium oxysulfate filter (SKC Inc., Palo Alto, USA)	active	0.04	0.01	mass spectrometry
TPP PDMS SPME-fiber (Merck KGaA, Darmstadt, Germany)	passive/diffusive	0.03	0.01	mass spectrometry

the concentration of the complex led to the formation of a yellow product with the highest absorbance observed at 410 nm, which was then evaluated on-site using a DR 1900 portable spectrophotometer (Hach Company, Loveland, USA) previous elution with 2 ml of H₂SO₄ 1M.

Air monitoring by a portable continuous direct reading detector was evaluated using:

- the ATI Series C16 PortaSens II portable gas leak detector (Analytical Technology Inc, Colleagueville, USA);
- the Interscan 4000 Series Compact portable analyzer (Interscan Corporation, Simi Valley, USA);
- the SafeCide portable monitoring system (ChemDAQ, Pittsburgh, USA);
- the Dräger X-am 5100 gas detection meter (Drägerwerk AG & Co. KGaA, Lübeck, Germany).

The technical data of the 4 portable instruments are shown in Table 1.

Dynamic calibration system

In order to obtain air samples containing known concentrations of HP, the authors made use of the dynamic system proposed in previous works [29–31] with some modifications. The Harvard Plus 11 syringe pump (Harvard Appara-

tus, Holliston, USA), equipped with a 1 ml gas-tight syringe set to 2 µl/min, connected to the Adsorbent Tube Injector System (ATIS) (Supelco, Bellefonte, USA), was used to generate HP vapor. All 6 samplers were simultaneously exposed to each HP air concentration, and for each one, 5 determinations were performed. The HP air concentration ($C_{\text{HP air}}$) was calculated using the following formula:

$$C_{\text{HP air}} = C_{\text{Sol}} F_{\text{syringe}} / F_{\text{air}} \quad (1)$$

where:

$C_{\text{HP air}}$ – the concentration of the analyte in the air (mg/l),

C_{Sol} – the concentration of the solution (mg/ml),

F_{syringe} – the syringe pump flow (ml/min),

F_{air} – the air flow (l/min).

The concentration of the water vapor produced by the impinger was determined by measuring the dew point temperature with the photoacoustic infrared Innova type 1312 multigas monitor (LumaSense Technologies, Milpitas, USA). Atmospheric pressure was determined with the GE Druck DPI 705 digital pressure indicator (General Electric, Boston, USA).

Statistical analysis

In Table 2, the authors reported the theoretical HP atmospheric concentrations tested, and the relative observed mean and standard deviation measurements for each method. The statistical analysis was conducted using Stata software release 11 (StataCorp LP). Simple regression models were performed to assess calibration between the theoretical and measured values, and the authors evaluated the hypothesis of “perfect calibration” ($H_0: \beta = 1, \alpha = 0$). They thus reported estimates of α and β with the standard error (SE) and the p-value, performing a hypothesis test with F statistics involving coefficient restriction. Finally, the r^2 value was calculated to verify the goodness of fit of the estimated regression model for each method.

Sampling sites

A survey carried out in wood pulp bleaching – estimated to hold the largest share of the industrial HP market – food and beverage disinfection processing, and a hospital department to reduce the risk of spreading nosocomial infections, was performed during routine operations to assess the risk of HP occupational exposure. Measurements of HP vapor were performed in the following industrial segments:

- pulp and paper manufacturing, during HP tank refilling,
- soft drinks manufacturing during servicing of a high-speed filling machine,
- hospital intensive care units after HP nebulization.

The BABUC/A multi-data logger (LSI Lastem, Milano, Italy) was employed to measure temperature, relative humidity and air velocity during air sampling.

RESULTS

Performance of the 6 methods

The analytical procedure combines the efficiency of fast GC/MS systems with both high automation throughput and the quantitative accuracy of SPME on-fiber derivatization.

This method allows for automated assays to be performed in very short time windows, characterized by higher sensitivity power (the theoretical and experimental sampling rate values [SRs] were 0.0397 ml/min and 0.0324 ml/min, respectively) and discrimination than other routine techniques employed in hygiene industrial laboratories, thanks to the structurally informative MS fragmentation pattern (Figure 1).

Calibration curves, simple regression parameters, and the limit of detection (LOD)/limit of quantification (LOQ) values were reported in Table 2. In particular, the TPP-PDMS-TWA-SPME fiber showed the lowest LOQ value (0.009 ppm) and the best goodness of fit ($r^2 = 0.999$) of the calibration with theoretical HP atmospheric concentrations. Given the level of significance expressed as a p-value of 0.05, the authors did not obtain any evidence to reject the null hypothesis (H_0) for all the 5 methods under evaluation.

Monitoring campaigns

The monitoring campaigns showed that the increase in HP could be relatively high: in particular, a HP concentration of up to 67 ppm was measured in food and beverage processing. The exposure scenarios presented in Table 3 are in line with the inference method [29] that may be applied to a substance with a full-shift limit value when the integrated air sampling is significantly lower than TWA and the STEL level has not been set. This consideration is especially important for HP because of its lack of biological monitoring and odor. As many as 6% of all measurements performed during bottle outfeed in food and beverage plants provided results close to the IDLH value.

DISCUSSION

This paper aims to support the development of HP work-related exposure limits by means of evaluation of human exposure in several key occupational settings. The authors suggest that occupational medicine could be a precious

Table 2. Calibration data of the analytical method and the direct reading systems in the laboratory dynamic calibration system in the study on hydrogen peroxide monitoring

Variable	Swinnex titanium oxysulfate filter	TPP PDMS SPME fiber	ATI Series C16 PortaSens II electrochemical sensor	ChemDAQ SafeCide portable monitoring electrochemical sensor	Interscan 4000 Series Compact 4090-199.9M electrochemical sensor	Drager X-am 5100 gas detection meter
Theoretical HP atmospheres (M±SD)						
0.08 ppm	0.12±0.06	0.07±0.01	0.1±0.05	0.1±0.04	0.1±0.08	0.3±0.40
0.16 ppm	0.15±0.04	0.17±0.01	0.1±0.01	0.1±0.05	0.1±0.05	0.1±0.00
0.31 ppm	0.28±0.08	0.32±0.02	0.4±0.21	0.3±0.16	0.3±0.11	0.3±0.15
0.62 ppm	0.60±0.08	0.61±0.04	0.5±0.07	0.5±0.04	0.7±0.19	0.8±0.08
1.25 ppm	1.12±0.08	1.27±0.04	1.6±0.26	1.6±0.18	1.4±0.38	1.2±0.13
2.50 ppm	2.96±0.10	2.38±0.11	3.0±0.08	2.9±0.50	3.8±0.93	2.1±0.29
5.00 ppm	5.89±0.20	5.43±0.58	4.1±0.33	4.0±0.30	6.7±1.11	6.9±0.97
10.00 ppm	9.08±0.24	9.73±0.42	9.1±0.24	12.2±0.60	13.0±1.35	12.8±0.95
20.00 ppm	23.64±2.02	20.64±0.59	16.0±2.45	16.4±1.34	15.6±3.90	16.8±1.44
40.00 ppm	35.98±3.10	38.70±1.20	36.0±3.10	-	45.0±8.72	-
80.00 ppm	86.11±2.57	80.71±0.66	90.1±4.58	-	68.6±2.16	-
Method parameters						
LOD	0.012	0.009	-	-	-	-
LOQ	0.040	0.03	0.1*	0.1*	0.1*	0.1*
repeatability [%]						
within session	6.1	5.2	6.5	7.4	6.1	5.8
inter session	7.9	6.8	8.9	8.0	9.1	9.4
Simple linear regression estimation (y = α + βx)						
R ²	0.9928	0.9995	0.9888	0.9557	0.9830	0.9395
β (SE)	1.050 (0.030)	1.002 (0.007)	1.087 (0.039)	0.871 (0.070)	0.930 (0.038)	0.906 (0.086)
α (SE)	0.180 (0.832)	0.025 (0.198)	-1.174 (1.112)	0.365 (0.326)	0.952 (1.076)	0.576 (0.669)
p (F test H0: α = 0, β = 1)	0.238	0.942	0.146	0.242	0.252	0.561

LOD – limit of detection; LOQ – limit of quantification.

* LOD defined by the manufacturer.

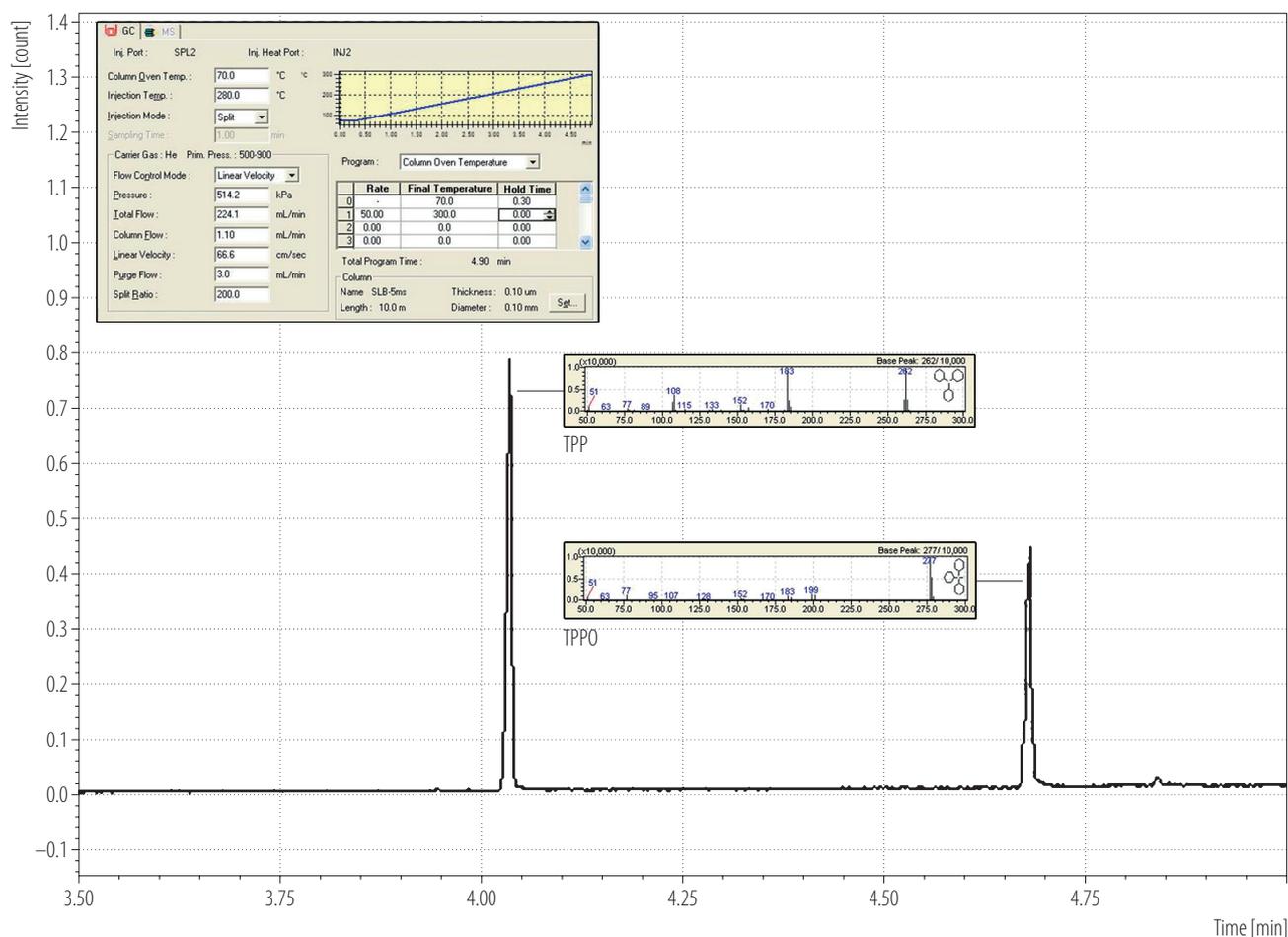


Figure 1. Gas chromatography conditions, chromatogram and fragmentation patterns of the triphenylphosphine (TPP) and triphenylphosphine oxide (TPPO) analysis in the study on hydrogen peroxide monitoring

contributor to the growth of exposure science, including also the problem of environmental contamination, thanks to the methods and knowledge derived from the investigations performed by the authors [32–35].

There is a growing use of HP as a sterilizing agent in industrial applications but its toxicity is often underestimated [36]. It tends to be overused, as a result of which significant amounts of HP frequently remain in the workplace atmosphere.

Data on the acute and chronic toxicity of HP are limited and outdated. Respiratory irritation symptoms have been reported among manufacturing plant workers exposed to HP. A single case of a long-term inhalation exposure

with dyspnea and bilateral diffuse nodular infiltrates on the lung has also been seen [37]. A survey of the health surveillance data on the production workers encompassed 110 workers, of whom 80 had been involved in the production for >10 years. The mean levels of HP revealed were <1 ppm whereas short-term concentrations were up to about 3.5 ppm, and about 7 ppm in accidental situations [38]. The Finnish Institute of Occupational Health conducted a study inside a company, focusing on a small group of workers exposed to HP vapor; peak exposures of up to 8 ppm (8-h TWA 2 ppm) of HP in the air were measured in the breathing zone of the individuals [39]. In line with the exposure assessment scenario specified in

Table 3. Summary of hydrogen peroxide (HP) personal sampling results determined by means of 6 methods evaluated in the study on HP monitoring

Facilities/ Operations	T* [°C]	RH* [%]	Measure- ments [n]	Hydrogen peroxide [ppm] (M (min.-max))														
				Swinnex titanium oxysulfate filter	TPP PDMS fiber	TWA-SPME fiber	Portasense A&T c16 electrochemical sensor	ChemDAO SafeCide electrochemical sensor	Intersean 4090-1999 electrochemical sensor	DragerX-am 5100 sensor	30-min exposure	8-h exposure	30-min exposure	8-h exposure	30-min exposure	8-h exposure		
Maintenance works in filling bottle machines for soft drinks	23	65	15	-	0.12 (0.08-0.24)	0.31 (0.09-0.38)	0.14 (0.14-0.25)	0.2 (0.1-0.3)	0.2 (0.0-0.21)	0.2 (0.1-0.3)	0.2 (0.1-0.3)	0.3 (0.1-0.4)	0.2 (0.1-0.2)	0.2 (0.1-0.3)	0.2 (0.1-0.3)	0.2 (0.1-0.3)	0.1 (0.1-0.3)	
food and beverage plant	22	63	18	-	0.10 (0.08-0.011)	0.13 (0.08-0.15)	0.12 (0.08-0.19)	0.1 (0.1-0.2)	0.1 (0.0-0.2)	0.2 (0.1-0.3)	0.2 (0.1-0.2)	0.1 (0.1-0.1)	0.1 (0.0-0.2)	0.1 (0.0-0.2)	0.1 (0.1-0.3)	0.1 (0.0-0.2)	0.1 (0.0-0.2)	
operator desk	23	63	14	-	1.81 (0.81-2.95)	2.56 (0.43-3.23)	1.65 (0.53-1.95)	2.0 (0.2-2.4)	1.3 (0.9-2.0)	3.2 (0.3-3.5)	1.25 (0.8-1.8)	3.0 (0.3-3.7)	1.4 (0.3-2.1)	2.9 (0.4-4.3)	2.9 (0.4-4.3)	1.4 (0.3-5.1)	1.4 (0.3-5.1)	
caps ejector	26	65	49	-	5.12 (2.95-7.04)	12.81 (1.85-67.12)	5.93 (2.42-8.12)	11.1 (2.5-59.7)	7.2 (1.9-9.6)	13.5 (3.3-55.3)	3.15 (2.8-7.6)	12.8 (1.9-58.8)	6.1 (2.5-9.1)	12.9 (1.9-57.8)	12.9 (1.9-57.8)	6.1 (2.5-8.4)	5.4 (2.5-8.4)	
Disinfection of the Infectious Diseases Department wards	23	54	46	1.86 (0.11-3.52)	-	1.52 (0.21-4.47)	-	1.9 (0.3-2.3)	-	2.2 (0.2-3.2)	-	2.3 (0.3-3.5)	-	2.3 (0.3-3.2)	-	2.3 (0.3-3.2)	-	
hospital rooms disinfection	room entrance	23	54	46	1.86 (0.11-3.52)	-	1.52 (0.21-4.47)	-	1.9 (0.3-2.3)	-	2.2 (0.2-3.2)	-	2.3 (0.3-3.5)	-	2.3 (0.3-3.2)	-	2.3 (0.3-3.2)	-
Truck driver during filling operations of HP tanks	room entrance after HP nebulization	23	54	46	1.86 (0.11-3.52)	-	1.52 (0.21-4.47)	-	1.9 (0.3-2.3)	-	2.2 (0.2-3.2)	-	2.3 (0.3-3.5)	-	2.3 (0.3-3.2)	-	2.3 (0.3-3.2)	-
wood pulp and wastewater plants	Truck driver during filling operations of HP tanks	23	54	46	1.86 (0.11-3.52)	-	1.52 (0.21-4.47)	-	1.9 (0.3-2.3)	-	2.2 (0.2-3.2)	-	2.3 (0.3-3.5)	-	2.3 (0.3-3.2)	-	2.3 (0.3-3.2)	-

HP refilling	16	49	21	-	0.08 (0.08-0.012)	0.13 (0.07-0.11)	0.09 (0.08-0.12)	0.1 (0.1-0.1)	0.0 (0.07-0.11)	0.1 (0.1-0.1)	0.1 (0.1-0.2)	0.1 (0.08-0.12)	0.0 (0.07-0.11)	0.2 (0.0-0.12)	0.2 (0.0-0.4)
HP refilling pipes removal	14	51	21	-	0.09 (0.06-0.014)	0.11 (0.08-0.12)	0.10 (0.08-0.14)	0.1 (0.1-0.2)	0.1 (0.09-0.12)	0.1 (0.1-0.2)	0.1 (0.09-0.10)	0.2 (0.1-0.3)	0.1 (0.0-0.1)	0.1 (0.07-0.2)	0.1 (0.0-0.10)
HP refilling pipes washing	17	48	20	-	0.07 (0.06-0.013)	0.13 (0.07-0.16)	0.10 (0.06-0.11)	0.1 (0.1-0.1)	0.1 (0.1-0.1)	0.1 (0.1-0.1)	0.1 (0.1-0.1)	0.1 (0.0-0.3)	0.1 (0.1-0.1)	0.2 (0.0-0.2)	0.1 (0.1-0.2)

* Values are provided for ppm to mg/m³ conversion.

EU Regulation No. 528/2012 [5], the field data presented by the authors of this paper show the possibility of having occupational exposure values even close to the IDLH. In their opinion, the current 8-h TWA limits for HP do not reflect the actual risk; STEL would, therefore, provide a much better protection.

Since there are few conventional methods of assessing HP exposure in the field of industrial hygiene, the authors decided to expand their considerations to methods for the determination of airborne HP environmental concentrations. These methods are almost always time-consuming since they require preconcentration, before the proper analysis, of the atmosphere to be analyzed in a suitable trapping solution, by resorting to appropriate solid or liquid-phase scrubbers, or to stripping coils or denuders. As regard the use of impingers, this method has several disadvantages, i.e., it is not particularly suited to personal sampling and its use often leads to the production of artifacts, which are bound to liquid phase production and decomposition [40,41]. Using the denuder as a sampling trap requires a coating procedure and extraction of the collected gases. Both these procedures are labor-intensive and require trained operators [42].

The analytical methods employed by the authors are fully automated and allow data management, from the indirect and direct reading methods through to dedicated software. All 6 samplers were employed remotely by the HP Data Storing System (Chromline, Prato, Italy) as much as possible to avoid operator variability or mistakes. The sampling data and their analytical results were then integrated into a laboratory information management system (LIMS, Bika Lab System, South Africa) which generates reports and analyzes historical data (Figure 2). Combining the rapid FFA-SPME 1-min device and the electrochemical instrument enabled the authors to identify the moments when peaks occurred throughout emissions. Specifically, comparing the repeated continuous monitoring data with the long- and short-term limit values

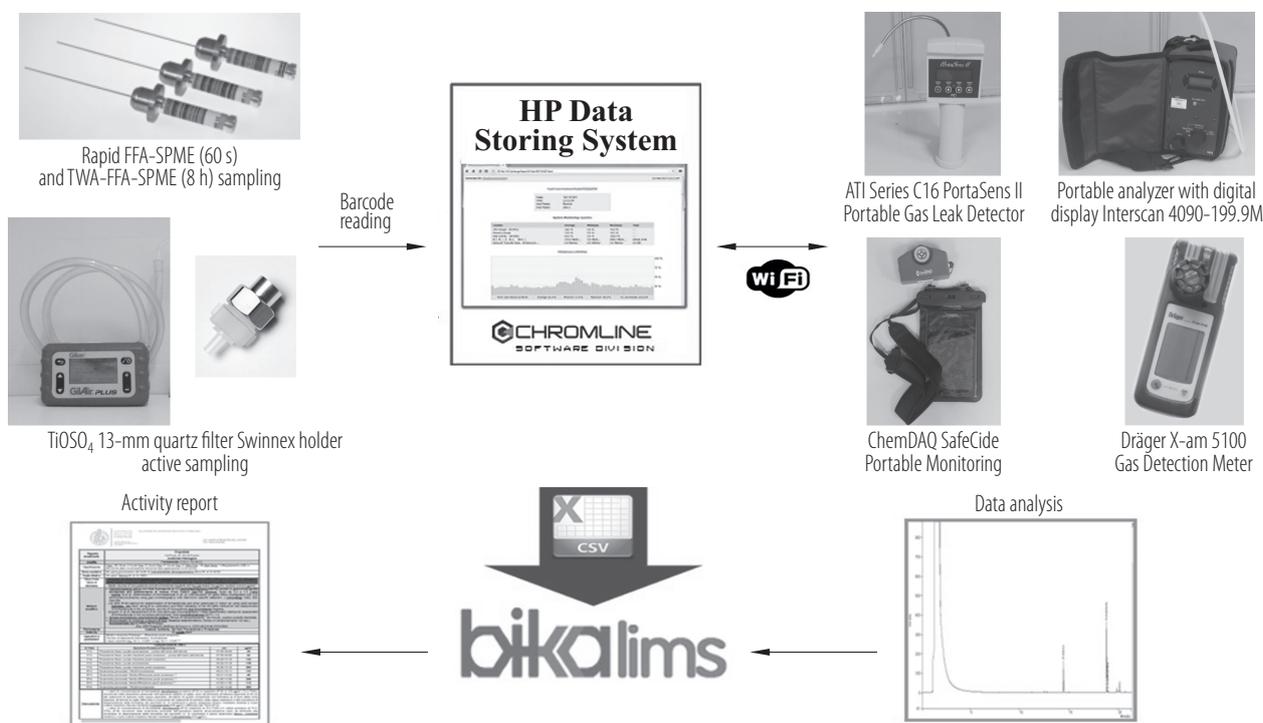


Figure 2. Laboratory information management system in the study on hydrogen peroxide monitoring

gave a picture of workplace exposure. On the downside, the rapid FFA-SPME requires a large number of fibers for sampling while the electrochemical sensors may have low specificity in certain conditions, but the SPME makes up for these shortcomings. The TWA limit values could be evaluated easily in terms of feasibility for operators by TiOSO_4 13-mm quartz filter Swinnex holder active sampling and TWA-FFA-SPME, which are both validated analytical methods.

Several approaches could be useful to test the calibration of methods from airborne compounds. The Bland-Altman plot [43] is usually adopted in clinical chemistry, and it is capable of assessing the consistency between 2 measurement techniques. The differences (or, alternatively, the ratios) between 2 techniques are plotted against their average values. Alternatively, the differences can be plotted against 1 of the 2 methods, if this method is considered a reference or “golden standard” method [44]. Otherwise,

the concordance of measurements performed with different analytical methods is commonly compared pairwise using Pearson’s test, evaluating the linear correlation between 2 variables [30,45,46]. Passing and Bablok [47] have described a linear regression procedure with no special assumptions regarding the distribution of the samples and measurement errors. The results do not depend on the assignment of the methods to X and Y. The slope and intercept are computed with their 95% confidence intervals (CIs). These CIs are then used to determine whether there is only a chance difference between the slope and 1, and between the intercept values and 0.

Herein, the authors have proposed a different hypothesis test with F statistics to compare the concordance between theoretical calibration atmospheres and measured values using different systems. The restriction of the α and β coefficients makes it possible to analyze the regression model in order to infer the compliance with the idea of

“perfect calibration” ($\alpha = 0$ and $\beta = 1$). According to the authors, this approach gives the advantage to evaluate the calibration of validated laboratory methods and direct reading instruments together, testing in the same condition of the measurements performed in the workplaces.

CONCLUSIONS

The aim of this work was to create an innovative monitoring approach measuring airborne HP concentrations in the workplace, which would be simple, fast and sensitive. To this end, 2 laboratory-based methods were evaluated with 4 commercially available direct-reading instruments, yielding comparable results. Unlike the TPP passive method which involves thermal desorption, the TiOSO₄ active sampling method requires chemical extraction before detection into a spectrophotometric unit. This problem is easily overcome by using SPME, a solvent-free technique that incorporates sampling, isolation and enrichment in 1 step. The derivatization kinetics showed that the reaction of TPP with HP was instantaneous during the sampling, and the SPME fiber retraction inside the needle allowed an excellent evaluation of TWA-occupational exposure limits. A database management system provided a central database that could be accessed by multiple users in a controlled manner. Its interface with Bika LIMS allowed for certain instruments, quality control, and ISO 17025 accreditation to be implemented, thus eliminating human error and reducing the costs of administration.

To conclude, the HP air monitoring protocol provides a remote integration of 6 monitoring systems in order to simplify sampling and analytic operations, setting the future bases for on-site analyses regarding second-level methods. In fact, as the number of different types of portable GC instruments with different complexity and capacity has continued to grow, the chromatographic method proposed is capable of being accepted by this technology. The authors recommend the simultaneous use of both

first- and second-level measurement methods; the choice of the instruments/methods to be adopted will be based on various factors, such as the financial resources available, the expected concentration and range values, the operator's experience, and the exposure scenario.

Moreover, due to the circumstances in which the TLV-TWA value is exceeded in normal use cases, a protocol to evaluate long- and short-term exposure to HP vapor is needed. The presented data show the possibility of having occupational exposure values even close to the 30-min IDLH limit. The monitoring campaigns showed that the increase in HP could be until 67 ppm and the 1 ppm current 8-h TWA limits for HP do not reflect the actual risk; STEL would, therefore, provide a much better protection. Exposures above the TLV-TWA values, and up to the TLV-STEL value, should not be longer than 15 min and should not occur >4 times/day, with a minimum interval of 60 min between exposures in this range.

The experimental and field comparisons showed that the aforementioned HP vapor measuring methods are consistent and can be easily integrated into an industrial hygiene plan to prevent significant acute toxicity resulting from HP vapor. Therefore, this protocol can be seen as constituting a reliable method for determining airborne HP concentrations in routine analyses.

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