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Ion mobility spectrometry evaluation of cocaine occupational exposure in forensic laboratories

Sergio Armenta [a,*], Miguel de la Guardia [a], Manel Alcalà [b], Marcelo Blanco [b], Clara Perez-Alfonso [c], Nieves Galipienso [c]

[a] Department of Analytical Chemistry, Research Building, University of Valencia, 50th Dr. Moliner St., E-46100 Burjassot, Valencia, Spain
[b] Department of Chemistry, Faculty of Sciences, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Barcelona, Spain
[c] Unidad de Inspección de Farmacia del Área de Sanidad de Valencia, Muelle de la aduana s/n, 46024 Valencia, Spain

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ABSTRACT

An approach, based on ion mobility spectrometry (IMS) has been developed for the control of cocaine in air of the breathing zone of operators, in laboratory surfaces and in nasal mucus of employees to evaluate cocaine exposure in a forensic laboratory. The analytical methodology has been validated in terms of accuracy, precision and limits of detection and results obtained were statistically comparable with those obtained by liquid chromatography. Cocaine concentration in laboratory air increases from 100 ± 35 ng m^{-3} of a normal day to 10,000 ng m^{-3} during the manipulation of cocaine seizures. The occupational exposure limit (OEL) for cocaine has not been established which difficult the evaluation of the health effects of continuous exposition to very small doses of cocaine. Cocaine was also found in almost all the analyzed sample surfaces and also was found in nasal mucus of the police officers that were present during the manipulation of cocaine seizures without using a face mask. In summary, cocaine concentrations could present a health hazard to the employees and therefore warrants remediation and some modifications of the manipulation operations have been proposed.

1. Introduction

Occupational safety and health can be defined as the area concerned with protecting the safety, health and welfare of people engaged in work or employment. The main goal of occupational exposure assessment programs is to eliminate contamination of the working environment in order to protect the health of workers or, at least, to keep contamination at as low a level as possible, below the exposure limit established by the competent authority or recommended by scientific bodies, by taking appropriate technical measures. The evaluation and control of the chemical exposure in the workplace are some of the major components of an effective occupational exposure assessment program.

It becomes especially relevant in the case of the pharmaceutical, agrochemical and chemical industries, where the protection of workers from the potential harmful effects of active pharmaceutical ingredients (APIs), pesticides and solvents and other chemical compounds is a significant challenge due to their potential toxicity. Unfortunate examples of the importance and necessity of adequate health and safety programs to prevent acute occupational-related illness regarding APIs [1], pesticide [2–4], textile paint components (Ardystil syndrome) [5], organic solvents [6] and heavy metals [7] exposure can be found in the literature.

In forensic laboratories, the personnel handle and, thus, are exposed to large quantities of ilicit drugs. Because of that, appropriate occupational exposure assessment programs are absolutely necessary to obtain information regarding passive exposure to illicit drugs and to propose measures to reduce the level of contamination as much as possible. However, there is only limited information on the effect of occupational exposure to illicit drugs and only a few number of reports have been published in the scientific literature [8–12]. In law enforcement settings, individuals in the immediate vicinity of seized evidence could inhale airborne cocaine dust or handling handle material contaminated with cocaine dust resulting in passive absorption [8]. Moreover, the potential for abuse drugs as cocaine [9,10] and methamphetamine [11] exposure in personnel producing dog training aids has been demonstrated. Recently, a report of the Department of Health and Human Services of the National Institute for Occupational Safety and Health (NIOSH) of the US stressed the problems associated with the passive exposure to illicit drugs of the employees during its manipulation and storage

* Corresponding author. Tel.: +34 96 354 40 04.
E-mail address: sergio.armenta@uv.es (S. Armenta).

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in forensic labs and vaults [12]. However, there is no previously published occupational exposure limit (OEL) for cocaine and, thus, it makes difficult the evaluation of the health effects of continuous exposition to very small doses of cocaine.

Procedures used to control workplace air safety frequently require the use of active or passive sampling followed by extraction and analysis by gas chromatography–mass spectrometry (GC–MS) [13] or liquid chromatography (LC) with MS detection [14] to achieve the selectivity and sensitivity required. In those methods, the time required for sample preparation and analysis typically means that results are available between one day and two weeks after sample collection. Thus, it implies that by the time a report is received, the worker may have already been exposed to excessive amounts of a hazardous compound, being completely useless the information provided.

Ion mobility spectrometry (IMS) is an analytical technique based on the gas-phase separation of ionized compounds under an electric field at ambient pressure [15]. The analytical potential of IMS, particularly as regards operational speed, atmospheric pressure operation, simplicity and sensitivity, offers viable alternatives in the determination of workplace air exposure with their own associated benefits which have not been fully exploited [16]. To our knowledge, there are only two precedents of the use of IMS as a tool for the occupational exposure prevention programs, both of them in the pharmaceutical industry [17,18].

This article reports the need to implement the occupational safety and health programs in forensic laboratories using IMS as a versatile, simple, fast and powerful tool to provide quasi real time data on drug exposure. We have used as an example a crime laboratory devoted to the analysis of seized illicit drugs in which those samples are received, sampled, analyzed and stored. The main objectives of the present study concern: (i) development of an integrated strategy for the occupational exposure assessment based on the IMS analysis of illicit drugs in air, surfaces and biological samples of employees and (ii) evaluation of the working environment conditions and suggestion of the measures of control whenever necessary.

The different testing parameters, including the concentration of illicit drugs in the personnel breathing zone [19], defined as the zone located within a ten inch radius of the worker's nose and mouth, surfaces [20] and nasal mucus of the operators [21] have demonstrated to be useful indicators to determine the potential risks of exposure of the employees and to evaluate the effectiveness of the procedural changes introduced in the laboratory and operators handling in reducing illicit drug exposure.

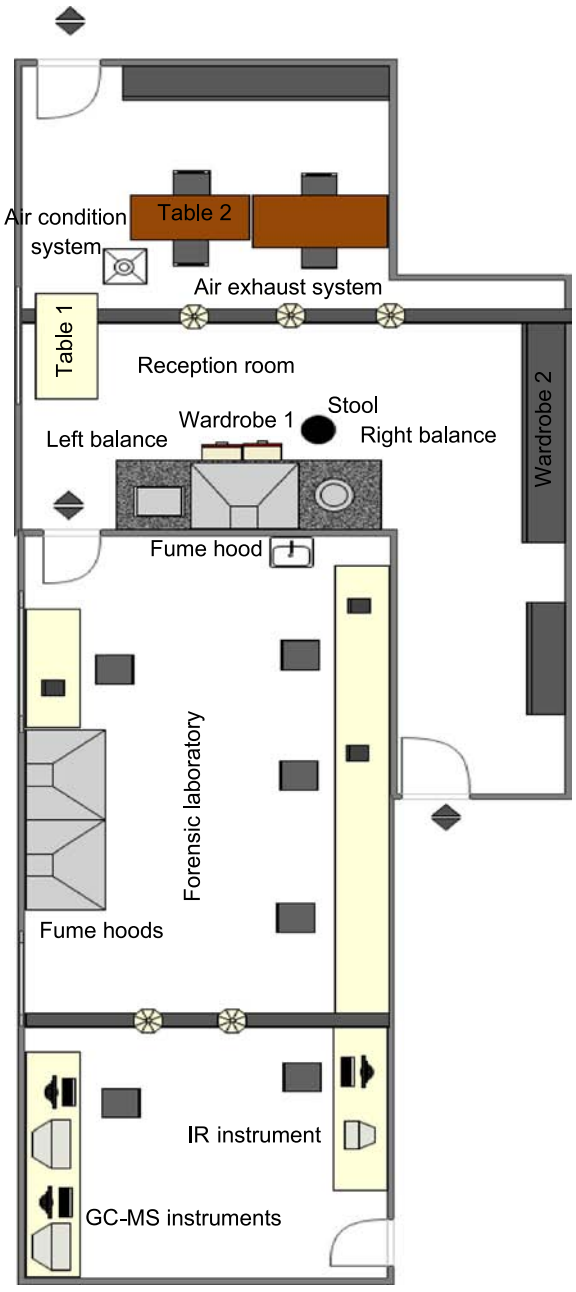

Fig. 1. Diagram of the forensic laboratory including seized simple reception room.

2. Materials and methods

2.1. Samples, reagents and standards

Illicit drug standard solutions, including cocaine hydrochloride dissolved in methanol at 1.0 mg mL^{-1} concentration level, were kindly provided by the "Ministerio de Hacienda y Administraciones Públicas" from the Spanish Government.

A calibration curve for cocaine hydrochloride, ranging from 0.02 to 100 mg L^{-1} and from 1 to 100 mg L^{-1}, was prepared by appropriate dilutions of the stock solution in isopropanol for IMS and LC analyses, respectively.

All the solvents used in this study were HPLC grade or higher. Methanol, isopropanol and acetonitrile were purchased from Scharlau Chemie S.A (Barcelona, Spain).

From September to December 2013, air, at personal breathing zone, laboratory surfaces and nasal mucus fluids were sampled in a public forensic laboratory. The laboratory diagram can be seen in Fig. 1. The laboratory itself is 42 m^2 and the reception room is 33 m^2. The reception room has two possible accesses through closed doors from either the adjacent office or a restricted corridor, while the laboratory can be accessed from the restricted corridor or the reception room. The forensic lab employees had workstations in the office area. An exhaust system placed in the reception area and also in the laboratory is continuously working, at a flow rate of approximately 10 times per hour, to remove contaminated air.

2.2. Air sampling

Air samples were collected inside the reception room, the laboratory and the two vaults by aspiration through polytetrafluoroethylene (PTFE) membranes of 4.62 cm diameter, 40 μm filter thickness and 2 μm pore size and a polypropylene (PP) supporting ring media obtained from Whatman Inc. (Florham Park, NJ, USA). The filters, specially manufactured for US EPA PM

2.5 Air Monitoring [22] with a minimum particle retention (0.3 μm) of 99.7% were mounted in a brass sampling head, with an effective sampling surface of 2 cm^2. Sampling was performed by a LABOPORT® mini diaphragm vacuum pump from KNF Lab (Freiburg, Germany) operated at 5 L min^{-1} flow rate for 10 min of aspiration time. The vacuum pump is a portable instrument (164 × 141 × 90 mm) 1.9 kg weight and 220 V/50 Hz power supply.

The compounds retained on the PTFE membranes were directly analyzed by IMS using thermal desorption without any sample treatment step. For the LC reference method, analytes were extracted from the PTFE membranes with 3 mL methanol. The solution was evaporated to dryness under dry air at room temperature and reconstituted in 50 μL acetonitrile, using limited volume inserts inside the standard chromatographic vials, supplied by Thermo Scientific (Rockwood, TN, USA).

2.3. Surface sampling

Surface contamination was evaluated in various laboratory surfaces; such as tables, wardrobes, balances, stool, shelf and drawers using Alpha® sampling swabs from Texwipe (Kernersville, NC, USA). They are double layer polyester swab specifically engineered for cleaning validation purposes. The swab handled is notched to snap off the head for convenient sample handling. It is important to note that the heads of the polyesters swabs used in this study were thermally bonded to the handles without adhesives, avoiding possible contamination during extraction. The swabs were also laundered by the manufacturer to minimize inherent non volatile residues or particulates that could affect the sensitivity of the analysis [23].

Prior to sampling, the swabs were wet via its immersion in a 2 mL isopropanol solution. Swabbing implies a systematic multi-pass of the soaked swab over the defined area always going from clean to dirty areas to avoid recontamination. In our case, we used 8 side by side strokes vertically, 8 horizontally and 8 each with the flip side of the swab in each diagonal direction. The soaked swab should be firmly passed and, after that, the swab stem was cut approximately 1 cm above the swab head and transferred to a 2 mL isopropanol vial. The isopropanol solution was analyzed by IMS and by the LC reference procedure.

In order to have additional information on the surface contamination study, mainly related to their identification, samples were also analyzed by infrared spectroscopy (IR) using the attenuated total reflectance (ATR) sampling mode. It employed a DuraSamplIR II accessory from Smiths Detection Inc. (Warrington, UK) equipped with a nine reflection diamond/ZnSe DuraDisk plate, installed on a Bruker FTIR spectrometer model Tensor 27 with a KBr beamspliter and a DLaTGS detector. The scanner of the interferometer was operated at an HeNe laser modulation frequency of 10 kHz. Spectra were recorded in the mid infrared region, from 4000 to 650 cm^{-1}, with a spectra resolution of 4 cm^{-1}, a zerofilling value of 2 and a Blackman–Harris 3-term apodization function, averaging 25 scans per spectrum.

30 μL of the isopropanol sample solution was placed in the ATR plate; the solution was evaporated to dryness using a nitrogen stream and the IR spectra were collected and compared with those of a library of illicit drugs and cutting agents.

2.4. Nasal fluid sampling

A double-ended cotton tipped, regular size swab with polystyrene handle was used for biological nose fluid collection. The swab was inserted into the nostril, approximately 2 or 3 cm, rotated twice (2 × 360° turns) collecting the biological fluid, slowly removed and finally it was inserted in a 2 mL amber glass vial containing 1.5 mL methanol. The polystyrene handle was cut and the vial was closed, named with an appropriate code and stored at −4 °C until analysis. The sampling was repeated by inserting the other swab end in the second nostril of the nose.

Mucus specimens obtained from employees of the crime laboratory and police officers keeping the seized samples were analyzed by IMS and LC procedures. All persons involved in this study were informed and provided their consent.

2.5. Ion mobility spectrometry procedure

A Smiths Detection IONSCAN-LS (Morristown, NJ, US) equipped with a ^{63}Ni foil radioactive ionization source, was used to separate and identify the different compounds involved in this study. IM station software (version 5.389) was used for data acquisition and processing. Plasmagrams were acquired in positive ion mode using nicotinamide, with a reduced mobility (K_0) of 1.860 $cm^2\ V^{-1}\ s^{-1}$, as internal calibrant. The number of segments per analysis was 56, every plasmagram containing 779 data points. The shutter grid width was 0.2 ms (the value optimized by the manufacturer) and plasmagrams were collected with a scan period of 40 ms. A counterflow of dry air, set to 300 mL min^{-1}, was introduced as drift gas at the end of the drift region. The electric field strength in the drift region was 252 V cm^{-1} with a total drift voltage of 1764 V and a drift tube length of 7 cm.

Thermal desorption of compound solutions from PTFE membranes was used for sample introduction. In this strategy the PTFE membrane was introduced in the desorption unit where it was heated and the analytes transferred to the ionization region. In the surface contamination study, one microliter of the sample solutions was placed onto the PTFE membrane and heated to vaporize the analytes which were transferred to the ionization region. Desorption, inlet and drift tube temperatures were adjusted to 260, 275 and 232 °C, respectively. Using a 10 s post-dispense delay, the sample tray containing the PTFE membrane was inserted in the heated zone and the sample was held in this position for 30 s. Before analysis, Teflon membranes are introduced into the IMS instrument to remove any possible interference.

2.6. Liquid chromatography (LC) reference procedure

The LC procedure for cocaine determination was adapted from [24]. An Agilent 1100 Series (Palo Alto, CA, USA) LC system equipped with a Kromasil 100 C18 column (250 mm × 2.0 mm, 5.0 μm) and a diode array detector, working in the absorption range from 200 to 400 nm, was used for chromatographic analysis. The column temperature was maintained at 28 °C and the most appropriate wavelength was selected for the determination of each analyte. In all the cases, an injection volume of 20 μL was selected for samples and standards. The LC gradient method consisted of the use of an acetonitrile/phosphate buffer (0.05 M, pH 3.0) mobile phase at a flow rate of 1 mL min^{-1}. The solvent program was as follows: initially, the mobile phase consisted of a mixture acetonitrile/phosphate buffer (0.05 M, pH 3.0) 16:84 v/v for 7 min, then a 3 min linear gradient to acetonitrile/phosphate buffer (0.05 M, pH 3.0) 95:5 v/v was applied and finally it was maintained during 6 min. After that, 2 min linear gradient to the initial conditions and finally 7 min in the initial conditions were applied.

3. Results and discussion

3.1. IMS plasmagrams of cocaine and other illicit drugs

The ion mobility plasmagrams of cocaine and other illicit drugs are depicted in Fig. 2 together with plasmagrams of samples

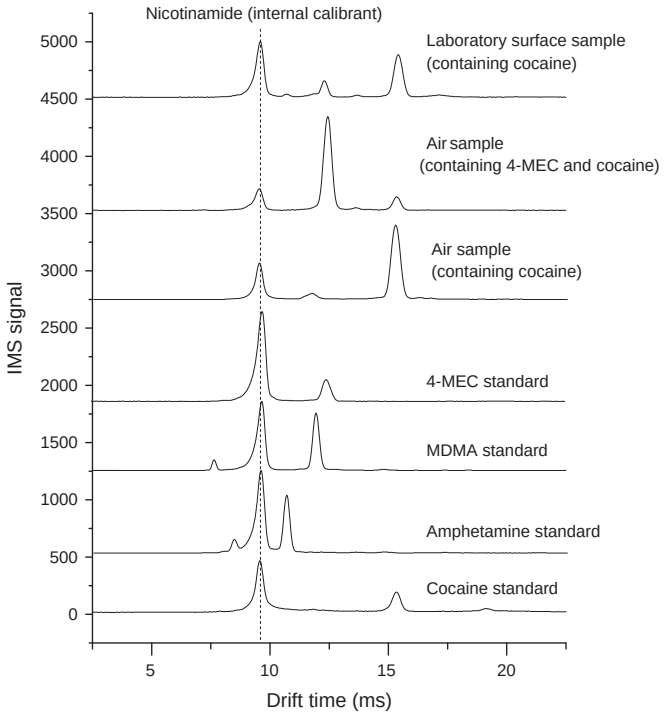

Fig. 2. IMS plasmagrams of cocaine and other illicit drugs together with those obtained for air and surface samples from forensic laboratories. 4-MEC: 4-Methylethcathinone and MDMA: 3,4-methylenedioxy-N-methylamphetamine.

collected during this study. The most intense peak in all plasmagrams is due to the internal calibrant, nicotinamide (K_0= 1.860 $cm^2\,V^{-1}\,s^{-1}$), used in the positive ionization mode to correct for variations in temperature, pressure and drift field and to increase the selectivity of measurements.

Although precise assignment of the plasmagram peaks needs a MS coupled to the IMS, it could be speculated that the main peak of the plasmagram, excluding that of the reactant ion, is due to the analyte molecular mass peak. Cocaine plasmagram provides a peak at 15.07 ms drift time with a reduced mobility of 1.16 $cm^2\,V^{-1}\,s^{-1}$, which is consistent with previously reported values [13,25,26]. Cocaine can be also identified in the plasmagrams of laboratory surface and air samples together with some illicit drugs usually manipulated in the forensic laboratory; such as amphetamine, 3,4-methylenedioxy-N-methylamphetamine (MDMA) and 4-methylethcathinone (4-MEC).

An alarm was generated to alert the presence of illicit drugs in the samples, using the following peak descriptors: (i) the K_0 value, for instance, cocaine 1.16 $cm^2\,V^{-1}\,s^{-1}$, (ii) a variability value of 50 μs of the peak drift time, to compensate for small changes of the expected K_0 value, (iii) a full width value at the half-maximum height (FWHM) of the peak of 200 μs, (iv) a peak amplitude equal or lower than 1.5 times the FWHM of the peak, 300 μs, and (v) a signal higher than the signal threshold value (10 arbitrary units).

3.2. Analytical features of the IMS procedure

Due to the fact that cocaine is the second most commonly used illicit drug in Europe overall and it is the drug most usually seized, weighed, sampled, transferred and manipulated in the forensic laboratory participating in this study, the quantitative part of this paper will be focussed on this analyte. However, it should be mentioned that the quantitative evaluation of other drugs, such as heroine, MDMA and 4-MEC, in the presence of cocaine in air of forensic laboratories would be also possible because the characteristic peaks of this drugs are not overlapped [27].

The analytical validation of the IMS method was performed in terms of linear range, linearity, precision and limits of detection and quantification. Quantification was based on the measurement of the peak area of the average plasmagram obtained from the IMS cocaine analysis. The calibration curve was linear in the ranges from 0.02 to 4 ng and from 4 to 100 ng, corresponding to the analysis of 1 μL of cocaine standard solutions from 0.02 to 4 mg L^{-1} and from 4 to 100 mg L^{-1}, with regression lines of $y=(5.2\pm0.7)+(12.6\pm0.3)x$ and $y=(72\pm6)+(1.57\pm0.11)x$ for the studied ranges and correlation coefficients higher than 0.99.

The precision of the method, established as relative standard deviation (%RSD) was evaluated by analyzing four replicates of 0.15 and 12.5 mg L^{-1} cocaine standard solutions, corresponding to an absolute amount of drug of 0.15 and 12.5 ng. Precision varied from 11% to 1.4%, depending on the concentration of cocaine in the solution.

The LOD was calculated as three times the standard deviation of the intercept divided by the slope of the calibration line. It was calculated a LOD value of 0.15 ng, which corresponds to 3 ng m^{-3} taking in consideration a sample air flow rate of 5 L min^{-1} and a sampling time of 10 min.

The accuracy of the proposed procedure was evaluated by comparison of the recovery percentage results obtained by IMS and by a LC reference methodology for the analysis of PTFE membranes spiked with cocaine concentrations from 20 to 100 ng. The Student's t for the comparison of the obtained results was lower than the tabulated values, implying that the accuracy of both methodologies is comparable. It should be highlighted that the analysis of spiked membranes by LC included the extraction of cocaine from the membrane with 3 mL of methanol, evaporation to dryness and reconstitution in 50 μL of acetonitrile.

Other figures of merit of the methodology that should be highlighted are the productivity (90 samples per hour, without considering sampling time) and reduced cost of analysis (~4€ per membrane). Moreover, the reagent consumption and waste generation were completely avoided and, consequently, the cost of acquisition of reagents and solvents and that of treatment of wastes were drastically minimized, thus reducing the environmental risks of the analytical steps.

3.3. Air samples

It is well known that during the sampling and handling of illicit drugs, airborne dust can be formed. Thus, to evaluate potential risks for the employees, air samples from 4 different workplace areas inside the institution were collected.

The developed IMS procedure allowed the identification of the drugs present in the workplace air samples using the spectral library. Cocaine was identified in all the air samples evaluated. On the other hand, other illicit drug; such as 4-MEC, was positively identified in the reception area air during sampling and handling of a white powder seized material which was identified as 4-MEC by GC–MS.

The employed methodology also allows the quantitative determination of the drugs in the forensic lab air samples. Table 1 shows the concentration of the identified illicit drugs in the workplace air analyzed. It should be mentioned that values of Table 1 corresponded to air sampled the same day with a sampling frequency of approximately 30 min. All air samples showed detectable levels of cocaine, reflecting airborne concentrations ranging from 56 to more than 10,780 ng m^{-3}.

The airborne levels of cocaine were considerably higher than any other drug we measured. Cocaine was present in all the air samples even if no cocaine seizure was handled during the sampling period and, thus, to understand better the potential sources of contamination and to evaluate the potential risk for the

Table 1
Cocaine concentration found by IMS in the laboratory workplace air.

		Cocaine concentration in air (ng m^{-3})
Laboratory	Sample 1	56
	Sample 2	64
Reception room	Sample 1	112
	Sample 2	116
	Sample 3	125
	Sample 4	139
	Sample 5	80
	Sample 6[a]	8728
	Sample 7[a]	10780
Storehouse 1	Sample 1	< LOD
Storehouse 2	Sample 1	8.8

[a] In these cases, sampling was performed during cocaine manipulation.

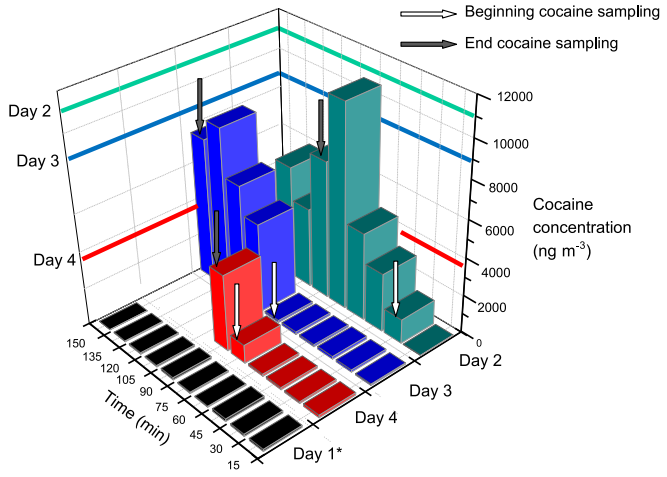

Fig. 3. Evaluation of cocaine concentration of the air of the reception room at different days, with and without cocaine seizures. Day 1: No cocaine seizure was manipulated this day in the forensic laboratory. Day 4: Some modifications such as replacement of filters in the fume hood and exhaust ventilation system and redesign of the laboratory to facilitate the cleaning of floors, machinery/instrumentation and furniture were adopted.

employees, a detailed studied regarding this analyte was performed. The air of the reception room was evaluated at different days, with and without cocaine seizures and the concentration of cocaine in the air samples, in ng m^{-3}, was calculated (see Fig. 3). It should be highlighted that most of the working operations were performed in confined areas and operators exposed to airborne dust wore filtering face piece class P3 (FFP3 masks), with a 99% airborne particles filter efficiency, and lab coats. Moreover, an independent air regeneration system was continuously working inside the reception area.

As it can be seen from results presented, the concentration of cocaine in the air of the reception room in a day without cocaine seizure (day 1) was around 100 ± 35 ng m^{-3} ($n=20$) and it increased considerably ($\times 100$) during the manipulation of cocaine seizures reaching concentration levels of 10,000 ng m^{-3} (days 2 and 3). The increase of cocaine concentration in the air samples was mainly due to the opening, transferring, sampling and resealing of cocaine packages. Moreover, a decrease of the concentration of cocaine can be found in day 4, mainly due to some modifications proposed and adopted such as appropriate replacement of filters in the fume hood and exhaust ventilation systems and redesign of the laboratory to facilitate the cleaning of floors, machinery/instrumentation and furniture among others.

Air cocaine concentrations in a day without large cocaine seizures were in the range of 100 ng m^{-3} (for perspective, whereas the OELs for substances such as aspirin or paracetamol are in the mg m^{-3} range, the majority of newer pharmaceuticals require controls that reduce workplace exposure to levels < 100 μg m^{-3}, with some in the subμg m^{-3} range) [18]. However, there is no previously published OEL value for cocaine and, thus, it makes difficult the evaluation of the health effects of continuous exposition to very small doses of cocaine. Additionally, it must be noticed that the concentration of cocaine in air extremely depends on the amount of samples handled.

3.4. Surface samples

Most of the laboratory operations like opening, transferring, weighing, sampling and resealing package, result in contamination of the working environment. So, the aforementioned operations are normally performed inside a fume hood located in the reception room to reduce as much as possible air contamination (see Fig. 1). Because of that, the fume hood can be considered the main focus of airborne particles generation and cocaine particles with a large size are deposited in its vicinity. Non-volatile chemicals, like cocaine is, remain on surfaces for long periods of time, being a potential source for skin absorption which can occur without being noticed by the employee and, in some instances, may be a more significant route of exposure than the respiratory system [28].

To evaluate contamination, different objects and surfaces, including tables, floor, digital balances, stools and wardrobes were sampled using a pre-wetted swab. As it can be seen from Table 2, cocaine was found on almost all the surfaces analyzed, ranging up to 104 ± 6 μg per 100 cm^2. Its concentration decreased as a function of the distance of the object sampled to the focus of the contamination, the fume hood.

Concentrations found by IMS were compared with those of the reference LC method. A linear function, $C_{IMS}=(2.1 \pm 1.2)+(0.94 \pm 0.03)\ C_{LC}$ with a regression coefficient $r^2=0.991$ ($n=12$)

Table 2
Cocaine concentration found in different surfaces of the reception and working room of the forensic laboratory.

	IMS cocaine concentration (μg/100 cm^2)	IR cocaine concentration (μg/100 cm^2)	LC cocaine concentration (μg/100 cm^2)
Left balance	104 ± 6	112 ± 5	105 ± 3
Right balance	8.6 ± 0.8	7.6 ± 0.8	5.8 ± 0.2
Stool[a]	11.0 ± 0.2	6.8 ± 0.9	13.6 ± 0.7
Table 1 (under window)	17.5 ± 0.6	23.1 ± 1.5	10.0 ± 0.9
Table 2 (reception desk)	< LOD	< LOD	< LOD
Table 3 (left balance)	29.8 ± 0.6	28.4 ± 0.8	29.7 ± 0.9
Table 4 (right balance)	20.0 ± 0.3	17.4 ± 0.5	22.0 ± 0.8
Wardrobe (under fume hood)	40.6 ± 0.7	ND	40 ± 5
Wardrobe 2 (shelf 5)	8.6 ± 0.3	11.6 ± 0.6	4.3 ± 0.7
Wardrobe 2 (shelf 4)	4.5 ± 0.3	< LOD	3.1 ± 0.3
Shelf and drawers (under fume hood)[a]	77 ± 9	78 ± 7	83.6 ± 1.5
Fume hood after cleaning	10.0 ± 0.9	9.8 ± 0.6	10.0 ± 0.4
Floor	29.72 ± 0.16	ND	31.7 ± 0.7

Note: analysis were performed in triplicate and the results are expressed as mean ± standard deviation.
< LOD: concentration of cocaine in the sample below the LOD of the technique (LOD_{IR}: 5 μg/100 cm^2 and LOD_{LC}: 0.8 μg/100 cm^2).
ND: not detected due to important interferences from other substances.

[a] The entire surface was sampled. The surface area was not determined, and hence, the results were expressed in μg/object.

was obtained. In that equation, the intercept and slope values were statistically comparable to 0 and 1, respectively, for a probability level of 95%, thus indicating that the developed procedure provided an accuracy comparable with that of the LC method.

Appropriate working operations and, as it can be seen in Fig. 3, adequate maintenance of the fume hoods and ventilation systems could contribute to reduce drug exposure of employees.

In order to have additional information on the surfaces contamination, mainly related to the identification of other substances, samples were analyzed by IR using the ATR sampling mode. The choice of IR spectroscopy as the second technique for analyte confirmation is due to its long history in illicit drug analysis [29], and the use of IR spectral libraries for the identification of abuse drugs [30]. However, sensitivity has been traditionally considered the Achilles Hell of the IR technique and, thus, this technique has been used to confirm the identity of the drug in those samples with a high concentration of cocaine. Fig. 4 shows the IR spectra of a cocaine solution (500 mg L^{-1}) and those of different surface swabbed samples. In those samples in which cocaine is present, typical absorption bands at 1726 cm^{-1} (stretching vibration of the carbonyl groups), 1271 and 1180 and 1115 cm^{-1} (acetate C–O stretching), 1071, 1029 and 1017 cm^{-1} (mono substituted benzene stretching and the last one an out-of-plane bending), 965 cm^{-1} (attributable to bending vibrations out-of-plane) and 715 cm^{-1} can be observed. Those IR bands perfectly match with previously reported cocaine IR spectra [31,32].

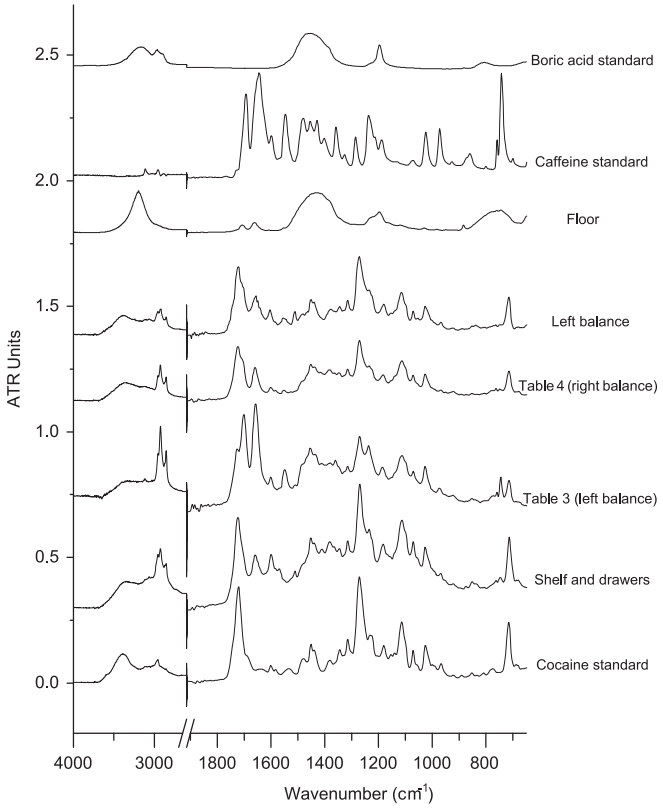

Fig. 4. IR spectra of a cocaine, caffeine and boric acid standard solutions (500 mg L^{-1}) and those obtained from different laboratory surface samples.

Moreover, in several samples (floor and wardrobe under the fume hood) the IR spectra was completely different from that of cocaine. By comparison of the obtained spectra with those of an IR library of illicit drugs and cutting agents, it can be confirmed that those samples were mainly composed by boric acid and caffeine, two substances usually employed by the drug dealers to increase their profits. Caffeine was present in other samples together with cocaine which can be confirmed by the presence of the two characteristic bands of caffeine at 1698 and 1650 cm^{-1}.

Although a specific legislation for cocaine surface contamination does not exist, it seems obviously desirable a reduction of those values to the minimum. Several US states have established feasibility-based surface contamination limits when remediating clandestine laboratories for methamphetamine ranging from 50 ng per 100 cm^2 to 500 ng per 100 cm^2 [33]. Levels of cocaine greatly exceeded the highest surface contamination limit for methamphetamine and considering that both of them are stimulants, the levels of cocaine surface contamination we measured could present a hazard to the employees and therefore warrants remediation.

3.5. Nasal mucus samples

As indicated in the Experimental part, a total of 33 nasal mucus specimens were collected from employees of the forensic laboratory and police officers keeping the seized samples. Samples of group I included five police officers responsible to custody seized samples at the beginning of sampling operations. Samples of group II consisted of the aforementioned police officers after sampling operations. It must be noticed that these subjects were not using protection masks. Samples of group III included four forensics assigned to work on a large cocaine seizure case consisting of 953 packages of 1 kg of cocaine. All the forensics were wearing a FFP3 face mask, a pair of latex gloves and laboratory coats. The complete time of 2–3 h were spent for inspecting, opening, transferring, weighing, sampling and resealing the 22 packages obtained by the application of the United Nations Office on Drugs and Crime recommended sampling criteria, $n = \sqrt{N/2}$ [34]. Nasal fluid mucus were collected after those operations. Samples of group IV consisted of five chronic cocaine consumers.

Table 3
Concentration of cocaine found by IMS in nasal mucus fluids of employees and visitors of the forensic laboratory obtained during a cocaine seizure manipulation.

Group I	Cocaine (μg/swab)	Group II	Cocaine (μg/swab)	Group III	Cocaine (μg/swab)	Group IV	Cocaine (μg/swab)
PO1A	ND	PO7A	0.056 ± 0.003	FE1A	ND	CC1	58.2 ± 1.8
PO1B	ND	PO7B	0.0257 ± 0.0013	FE1B	ND	CC2	176 ± 2
PO2A	ND	PO8A	0.64 ± 0.03	FE2A	ND	CC3	182.8 ± 1.4
PO2B	ND	PO8B	0.108 ± 0.007	FE2B	ND	CC4	172 ± 2
PO3A	ND	PO9A	0.32 ± 0.04	FE3A	0.013 ± 0.007	CC5	270 ± 13
PO3B	ND	PO9B	0.23 ± 0.13	FE3B	ND		
PO4A	ND	PO10A	1.01 ± 0.04	FE4A	0.612 ± 0.007		
PO4B	ND	PO10B	0.61 ± 0.04	FE4B	0.045 ± 0.006		
PO5A	ND	PO11A	0.302 ± 0.015				
PO5B	ND	PO11B	0.021 ± 0.003				

Note: analysis was performed in triplicate and the results are expressed as mean ± standard deviation.

As it can be seen in Table 3, nasal mucus of group I presented cocaine levels below the LOD of the technique. However, after the cocaine seizure manipulation, samples of group II, belonging to police officers exposed to the different operations without FFP3 face masks, presented levels of cocaine between 0.021 and 1.01 μg per swab. Comparing the concentration of cocaine found in those samples with that of cocaine chronic consumers (between 58 and 270 μg per swab), the difference between both groups is evident and there is no doubt on the absence of cocaine effects on these subjects. However, it clearly shows that they were exposed to cocaine through the respiratory system. On the other hand, only in three samples of group III, cocaine was detected with concentrations between 0.013 and 0.612 μg per swab, which probably indicates that the face mask was not properly used.

From the aforementioned data, it is evident that people present during cocaine operation were exposed to the drug, being, thus, necessary to wear appropriate protection equipment during cocaine manipulation operations. Moreover, although the measured exposure levels were relatively low, some modifications or implementations of manipulation operations should be introduced to reduce exposures to cocaine as much as feasible.

4. Conclusions

Regarding the analytical methodology it can be concluded that results obtained through this study demonstrated that the IMS technique can be successfully used for workplace air monitoring in forensic laboratories. Sensitivity, in the ng–pg range, selectivity and results in near real time are important properties that ratify IMS as a serious alternative method in occupational exposure assessment. Moreover, IMS reduces analysis costs by reduction of the necessary time and skills as well as the need for disposing of solvent waste compared to chromatographic techniques. The different tested parameters, including the concentration of cocaine in air in the breathing zone, in laboratory surfaces and nasal mucus of operators and visitors, have demonstrated to be useful indicators to determine the potential risks of the exposure of the employees providing a general and complete picture of the forensic laboratory situation, suitable to be used for establishing an appropriate normative. It is clear that, the information provided by the different sampling techniques is complementary. Cocaine concentration in the breathing zone and in laboratory surfaces provides information on the amount of drug that could be inhaled or absorbed through the skin by the operators. On the other hand, cocaine concentration in the nasal mucus, especially compared to the amount found in the mucus of cocaine consumers, provides information on the dimension of the problem regarding health or habituation hazards of the employees.

Regarding the results from the forensic laboratory it can be concluded that even though the concentration of cocaine in air, in a normal day, and nasal mucus samples is not excessive, it is wise to reduce exposures to all drug particles as much as feasible. So far as possible, operations likely to result in contamination of the working environment should be isolated from the remainder of the premises so as to reduce the number of persons exposed. According to the results obtained through this study and from a general perspective, the following recommendations should be adopted in any forensic laboratory to prevent or limit the release of potentially harmful substances: (i) the opening, transferring, weighing, sampling and resealing of cocaine packages should be performed inside well vented fume hoods and the use of local exhaust ventilation situated as close as possible to the source of contamination. Original envelops of cocaine should be sealed inside plastic garbage bags also inside the fume hood to avoid the contaminants reach the breathing zone of the workers. (ii) Workers and police officers exposed to contamination hazards should wear appropriate respiratory protection and gloves. (iii) Workrooms and laboratories should be designed and maintained in such a manner as to reduce as far as possible surfaces on which waste might accumulate and to facilitate the cleaning of floors, machinery/instrumentation and furniture. (iv) Replace particulate filters in the fume hood and exhaust ventilation system according to manufacturer guidelines. (v) Changing out personnel at short, regular intervals while working with large cocaine seizures to reduce the occupational exposure to the drug.

In short, the present study has provided preliminary results to be taken into consideration for the development of good laboratory practices to avoid, as much as possible, occupational exposure to illicit drugs in forensic laboratories.

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