Detection of airborne cocaine and heroin by high-throughput liquid-absorption preconcentration and liquid chromatography–electrochemical detection

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ABSTRACT

A high-throughput liquid-absorption preconcentrator (HTLAP) for rapid and/or ultrasensitive detection and analysis of trace contaminants samples air at a rate of 600–700 l/min and collects analytes from vapors or aerosols at an efficiency of 40–60% into a small volume of liquid absorbent dripping at a rate of 0.1–2 ml/min. These features combine to reduce the lower detection limit (LDL) of available analytical instrumentation by a factor of > 1000 and/or to permit faster sampling and far more rapid on-site air monitoring than were previously practicable. LDLs of *ca.* $1:10^{13}$ (v/v) of alkaloids have been achieved with LC and electrochemical detection. The HTLAP is directly adaptable to most liquid-phase analyzers. The small rate of liquid collection is also compatible with available interfaces to mass spectrometers. Moreover, the HTLAP permits detection and quantitation of polar or highly reactive compounds that cannot be readily analyzed by conventional preconcentration and GC.

INTRODUCTION

The purpose of this work was to develop and evaluate a high-throughput liquid-absorption preconcentrator (HTLAP) that could facilitate detection of very low concentrations of trace air contaminants, such as those emanating from concealed low-vapor-pressure drugs or explosives. The focus was on the preconcentration of airborne cocaine and heroin, whose equilibrium vapor pressures at 20°C are about $1.0 \cdot 10^{-10}$ bar and $4 \cdot 10^{-13}$ bar [1], corresponding to 100 ppt (v/v) (pptv) and 0.4 pptv, respectively. The availability of an effective HTLAP might facilitate detection of drug contraband, especially in enclosed cargoes, or of concealed explosives, especially in an aircraft.

Various liquid-absorption-type air scrubbers are available [2–4] that preconcentrate air contaminants and provide an interface between air samples and liquid-phase analyzers, such as liquid chromatographs or colorimeters. However, few of these devices are designed for a throughput (*i.e.*, air-sampling rate) of > 1 l/min.

While this preconcentrator was being developed and challenged with cocaine and heroin vapors, a somewhat different HTLAP, developed independently for vapors of explosives, was being challenged by 0.1–0.5 pptv of trinitrotoluene [5]. This device uses much larger liquid volumes and achieves

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several times lower collection efficiencies than those reported here. Also being developed are dry high-throughput preconcentrators in which the analyte from a large volume of air is first adsorbed onto wall surfaces, then thermally desorbed into a small volume of carrier gas. Such preconcentrators may operate fast enough in conjunction with a mass spectrometer or ion mobility spectrometer to permit rapid screening for explosives that may be concealed on persons or in baggage. However, utmost sensitivity would be assured by operating an ultra-high-throughput preconcentrator for a longer time, e.g., for 10 min rather than 6 s so as to extract 100 times more analyte at a given sampling rate, e.g., while an aircraft is preparing for takeoff. In such applications, the adsorption sites at the surfaces of the dry high-throughput preconcentrators might get saturated within the first min, especially if interfering adsorbates are present in relatively high concentrations.

Although this study was restricted to the detection of cocaine and heroin, the results may be appli-cable to the detection and monitoring of other compounds, many of which are of environmental concern.

EXPERIMENTAL

Vapor generation

Measuring the collection efficiency for vapors of semivolatile compounds required an efficient and reliable vapor generator that could permit easy replenishment of test material between experiments and preparation of known concentrations of air-vapor mixtures (Fig. 1). A Neslab thermostat bath was set to the desired vapor pressure of the test material in accordance with a phase diagram that was derived from published data [1]. A stream of temperature-equilibrated carrier gas (nitrogen), flowing at an adjustable rate, served to control the rate of sublimation of solid test material in a disposable sample tube (4 cm long × 4 mm I.D.) containing a plug of silanized glass wool, and thereby yielded the desired concentrations of the tested vapors. Before
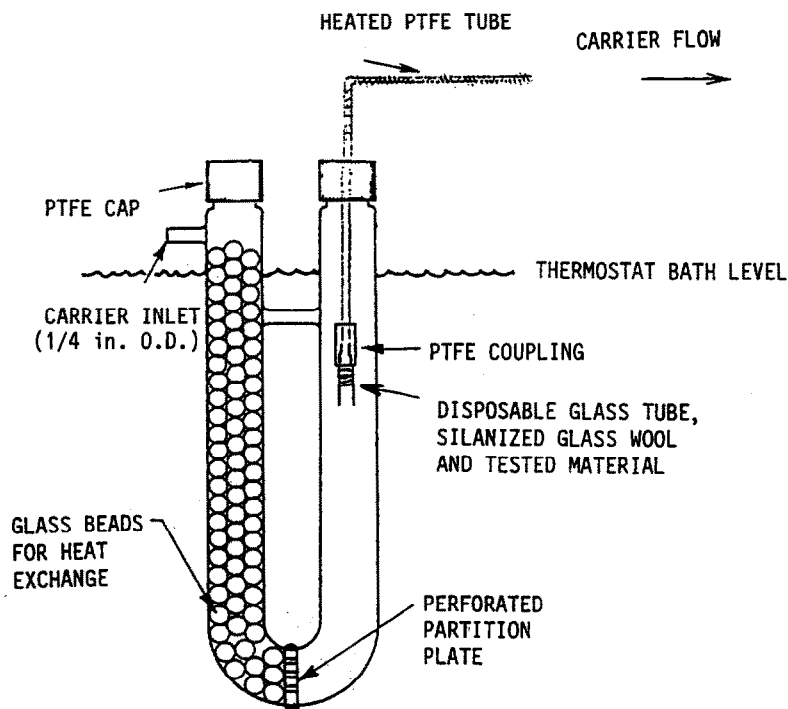

Fig. 1. Cross-sectional view of the U-tube contents of the vapor-generation apparatus. The carrier gas (nitrogen) passes at a rate of 0.5 l/min through a disposable glass tube containing a silanized glass wool plug impregnated with 0.1–1 mg of cocaine or heroin. 1 in. = 2.54 cm.

insertion into the U-tube, the glass wool was impregnated with a dichloromethane solution of 0.1–1.0 mg of the tested substance. The dried sample tube was then inserted into a PTFE coupling which connected the tube to an external 6 mm O.D. 4 mm I.D. PTFE perfluoroalkoxyl tubing (Catalog No. 6375-02, Cole Palmer Instrument Co., Chicago, IL, USA) that delivered the vapor-containing carrier to the preconcentrator inlet. To prevent analyte adsorption onto surfaces of the external tubing, the latter was uniformly wrapped with nichrome wire whose ends were plugged into a Variac transformer. The Variac was adjusted so as to yield a steady-state thermocouple reading on the inside of the tube that was at least 20°C above the temperature of the bath. Furthermore, the flow-rate of the carrier gas (0.5 l/min) was found to be 2–3 times higher than that yielding nearly saturated vapor, which further minimized any tendency for the analyte to condense or be adsorbed at the heated walls.

Analytical method

The analyses were performed by liquid chromatography (LC) with electrochemical detection (ED) [6]. The following general conditions applied to all the analyses: mobile phase, potassium phosphate buffer (pH 7–7.4, 0.02 M total phosphate)–acetonitrile (40:60, v/v); flow-rate, 1.0 ml/min, isocratic; solvent-delivery system, Waters (Milford, MA, USA) Model 6000 pump and Rheodyne Adsorbosphere HS C_{18} 25 cm × 4.6 mm cartridge (Alltech, Deerfield, IL, USA); electrochemical cell, Bioanalytical Systems (West Lafayette, IN, USA) LC/4B amperometric detector with a glassy carbon working electrode set at a potential of 1.0 V *versus* a Ag/AgCl reference electrode.

Collection efficiency measurements

To verify the vapor generation rate, the U-tube effluent was fed into a solid sorbent tube [Supelpak 204 (particle size, 0.06–0.12 cm), ORBO-40, Supelco, Bellefonte, PA, USA] for 30–60 min. The analyte was eluted from the sorbent tube with acetonitrile and quantitated by LC–ED. Independent tests confirmed that the sorbent tubes collected cocaine and heroin vapors at nearly 100% efficiency.

Analyses of sorbent tubes before and after each test were used to calculate the upper, lower, and average values of the HTLAP's collection efficien-

cy. The absorbates collected from the HTLAP were usually pretreated to eliminate or minimize interferences picked up from the sampled air and to gather the collected analyte into a smaller (0.5-ml) volume of liquid, ready for injection into the LC–ED system. The collected absorbate was first passed through a Sep-Pak C_{18} cartridge (Cat. No. 23501, Waters). The analyte was extracted from the cartridge with 3 ml of diethyl ether and, after evaporation of the ether, was redissolved in 0.5 ml of acetonitrile. In each case, chromatographic peak areas for collected samples were compared with those obtained in the same manner with tested solutions of known concentrations.

Preconcentrator materials and dimensions. An earlier preconcentrator design [7] was modified as shown in Fig. 2. A Pyrex glass tube, 56 cm long, 60 mm I.D., had an elliptical air inlet hole centered at 10 cm from its lower edge, a liquid distributor wheel located 6 cm below its upper edge, and a polyvinyl chloride plug with a 2.5 cm deep funnel-shaped cavity at the lower edge. A 6-mm-diameter hole at the center of the cavity abutted an external nipple that could be either closed off, to permit accumulation of liquid in the cavity during a sampling test, or left open, to permit collection of the liquid in different vials at selected time intervals.

Other components and accessories. The liquid absorbent was supplied by an adjustable metering pump (Model RPG-20, Fluid Metering, Oyster Bay, NY, USA). Adequate air suction was provided by a ring compressor (Model VFC301P-5T, Fuji Electric Corp. of America, New York, NY, USA). The air-sampling rate was measured by a rotameter (Model K72-10-0111, King Instrument Co., Huntington Beach, CA, USA) that was connected to the outlet of the ring compressor.

Liquid absorbent. The liquid absorbent was an aqueous solution of 0.1 g/l of Triton X-100 (Catalog No. 3555-4＊NY, Baxter Healthcare, McGaw Park, IL, USA) either acidified with 0.01 M H_3PO_4 or kept neutral with a 0.01 M sodium phosphate pH 7 buffer.

Operation of the preconcentrator. The air sampling rate was varied over the range of 550–700 l/min, the preferred range being 620–680 l/min. Higher flow-rates resulted in observable entrainment of liquid absorbent, whereas lower rates yielded reduced collection efficiencies (presumably associated
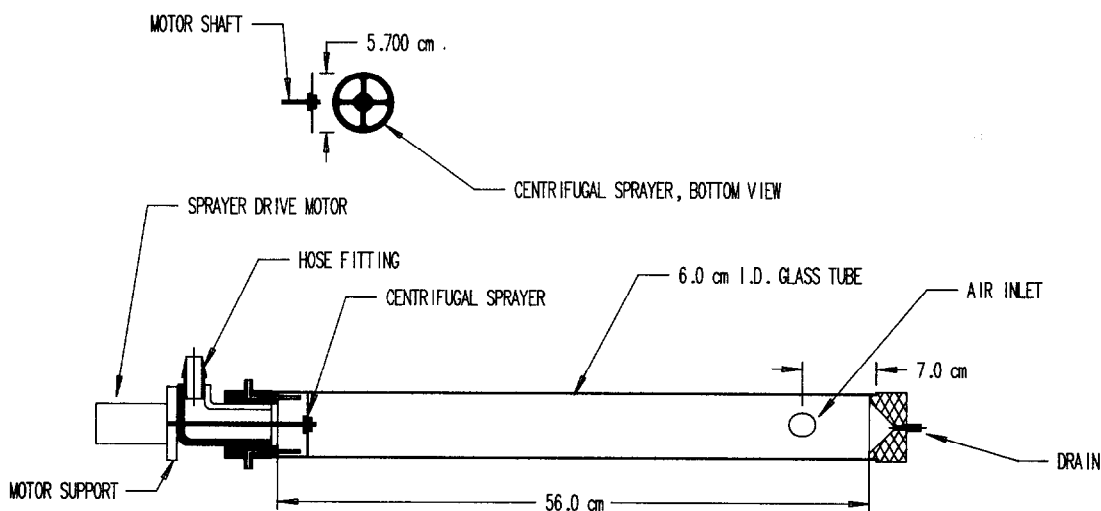
Fig. 2. Experimental high-volume liquid-absorption-type preconcentrator sampler. Air, at a rate of 700 l/min, passes through the 6.0 cm I.D. tube in a swirling, highly turbulent motion, which assures rapid transfer of trace constituents to a liquid film which covers the inner walls of the tube and is drained from the bottom at a rate of 0.1–1 ml/min.

with decreased air turbulence). The air flow in the HTLAP was highly turbulent and swirling, assuring rapid interchange of trace constituents between the air and the liquid film that covered the inner wall of the preconcentrator tube. The suction of the ring compressor generated a partial vacuum at the tube inlet that interfered with the drainage of absorbent from the bottom of the tube. To effect drainage, collection vials were enclosed in a tight container that was connected to the suction of the compressor. Use of Triton X-100 as wetting agent permitted reduction of the input rate of the absorbent to only about 1.0 ml/min while still maintaining acceptable wetting of the inner walls of the tube. Evaporation of water from the liquid film helped minimize the volume of collected absorbent, which was usually in the range of 3–5 ml for sampling times of 10–60 min.

Flow dynamics and optimization of air intake. The flow dynamics and collection efficiency of the pre-concentrator are greatly influenced by the size and geometry of the air inlet. To assure that the entering air follows a swirling path (which results in swirling of the extractant, full wetting of the inner walls, and efficient analyte transfer from the air to the absorbent), a 0.08-cm-thick sheet of PTFE having a 2.7-cm-diameter hole was taped over the air inlet hole in the Pyrex tube so that the holes partly over-

lapped. By trial and error, the most pronounced swirling was obtained when the hole centers were displaced as shown in Fig. 3. This air inlet config-uration was used in the latest tests and yielded im-proved collection efficiencies (see Fig. 4).

Also measured was the minimum drip rate at which the absorbent could be continuously collect-ed, while maintaining the inner walls at least 80% wetted. The minimum drip rate was as low as 0.06 ml/min. The drip rate can be increased at will, pref-erably to 0.1–2 ml/min, by increasing the liquid in-put rate.

RESULTS AND DISCUSSION

Collection efficiencies

The results of the collection efficiency measure-ments are shown in Fig. 4 for analyte concentra-tions of 0.1–150 pptv. There is no evident tendency for the collection efficiency to change with analyte concentration, type of analyte (cocaine or heroin) or acidity of the absorbent. For measurements per-formed before optimization of the air intake (Fig. 4) the root-mean-square value of the collection effi-ciency is nearly 40% (lower dashed line). After opti-mization, that value apparently increased to about 60% (upper dashed line, Fig. 4), but the apparent increase needs to be confirmed by more experimen-
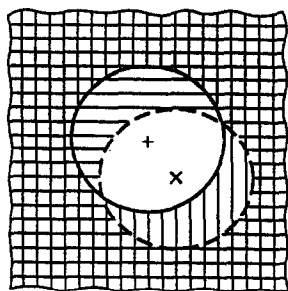
Fig. 3. Optimized air intake of the preconcentrator. Shading: vertical lines = PTFE sheet; horizontal lines = Pyrex wall. Symbols: × = center of elliptical hole in Pyrex (horizontal 2.7-cm major axis; vertical 2.5-cm minor axis); + = Center of circular 2.7-cm-diameter hole in PTFE (displaced relative to the × -marked center by 0.7 cm upward and 0.5 cm to the left).

tal data. The wide scatter of the experimental points may be due to analytical errors associated with background interferences, to unexplored variables (variations in air and liquid flow-rates, absorption of analyte by the plastic plug, etc.), and to a non-optimal configuration of the air intake.

The background interferences arose from two sources —contaminated laboratory air and impurities in the sorbent tubes. To correct for these conta-

minants, blank absorbent samples (obtained by sampling the laboratory air without injection of analyte) were spiked with known concentrations of the tested analyte, and the resulting chromatographic peaks were matched with those obtained in a preceding or following collection efficiency test. Such matching assumed that the contaminants in the ambient air remained the same during a 3-h period that included the collection of: (a) a first blank sample (60 min), (b) an analyte-enriched absorbent (60 min) and (c) a second blank sample (60 min). Variations in contaminants during the 3-h period could have resulted in either high or low values of the measured collection efficiencies, especially for the lower analyte concentrations (< 1 pptv).

Short-duration experiments. The two experimental points of Fig. 4 obtained for an analyte concentration of 114 pptv represent the results of short-duration measurements at two different drip rates, as detailed in Table I. Under the heading "Initial drip" (3rd to 5th columns) are the data for the first 0.5 or 1.0 ml of extractant collected during the first 30 or 15 s after introduction of the generated cocaine vapor into the air intake of the preconcentrator. The collection efficiencies measured for these initial samples are comparable to those for the extractant
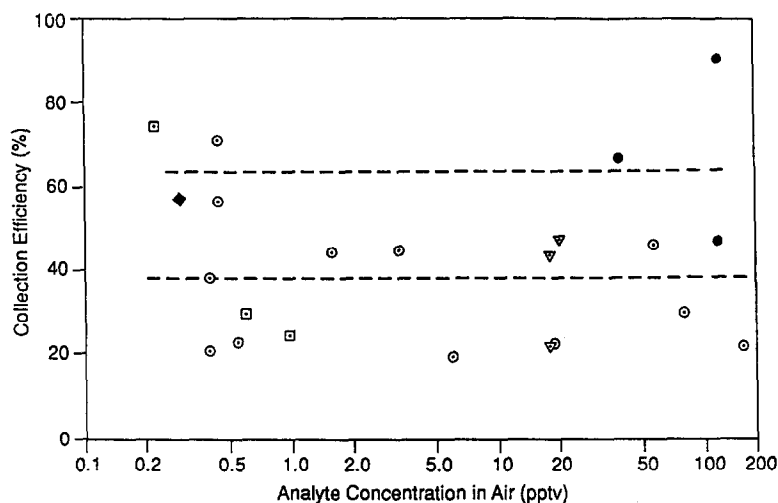

Fig. 4. The efficiency of collection of cocaine or heroin vapors using 0.1 g/l Triton X-100 in the extractant. □ = Heroin vapor collected by acidic extractant (0.01 *M* phosphoric acid); ∇ = cocaine vapor, same acidic extractant; ○ = cocaine vapor, neutral extractant (0.01 *M* pH 7 sodium buffer). ◆ = heroin vapor, same neutral extractant, after optimizing the air intake according to Fig. 3; ● = cocaine vapor, same neutral extractant, with optimized air intake. Lower dashed line: least root-mean-square (rms) collection efficiency for results obtained before intake optimization (open symbols). upper dashed line = least rms collection efficiency for results obtained after optimization of the air intake (filled in symbols).

TABLE I

RESULTS OF SHORT-DURATION COLLECTION EFFICIENCY MEASUREMENTS AT TWO DIFFERENT DRIP RATES

Drip rate (ml/min)	Cocaine vapor generation rate (µg/min)	Analyte collected from:												
		Initial drip			Continuous drip			Preconcentrator wall surface			All sources		
		Time (min)	Weight (µg)	Collection efficiency (%)	Time (min)	Weight (µg)	Collection efficiency (%)	Time (min)	Weight (µg)	Collection efficiency (%)	Time (min)	Weight (µg)	Overall collection efficiency (%)
1.0	0.98	0.5	0.11	35	8.5	6.3	76	9.0	1.54	17	9.0	8.0	91
4.0	0.98	0.25	0.25	103	4.75	1.8	39	5.0	0.23	5	5.0	2.3	47

collected immediately afterward under the heading "Continuous drip" (6th to 8th columns), i.e., 35–103% as compared with 39–76%. The high value of 103% is probably due to a timing error, as a time difference of 5 s, i.e., 20 s in lieu of 15 s, could have reduced the computed collection efficiency by 25%, i.e., from 103 to 77%. The comparable collection efficiency values for the initial drip and continuous drip measurements imply that a whiff of analyte collected by the preconcentrator over a brief time interval (ca. 10 s) should show up in the drip sample immediately after collection. This suggests that this preconcentrator may also be useful for rapid screening of passengers or baggage at airports and other ports of entry.

The tenth and eleventh columns of Table I indicate that, after a sampling run of 5–9 min, only a small fraction of the analyte collected by the liquid extractant is retained in the liquid film along the preconcentrator surface for drip rates of 1–4 ml/min. As expected, this fraction decreases with increasing drip rate, amounting to about 17%/91% = 19% and 5%/47% = 11% for drip rates of 1.0 and 4.0 ml/min, respectively.

Aerosol collection. To measure the HTLAP's ability to pick up aerosols, a corn oil mist (0.3–3-μm droplets) was produced by a Laskin nozzle, set at a pressure of 0.83 bar. The relative concentrations of these droplets at the preconcentrator inlet and outlet were measured with a Model TDA-2EL light-scattering photometer (Air Techniques, Baltimore, MD, USA). The photometer readings yielded an aerosol collection efficiency of 42–48%. This result was obtained before the optimization of the air intake and falls within the range of values of Fig. 4.

Potential applications

Estimated sensitivity enhancement. The mass W_i of analyte collected for various analyte concentrations in sampled air, should vary with sampling time approximately as shown in Fig. 5. For example, air containing 0.1 pptv of analyte, corresponding to about 0.1% of the equilibrium vapor pressure of cocaine or 20% of that of heroin at room temperature when sampled for 10 min, yields 4 ng of cocaine or 5 ng of heroin in the liquid extractant according to Fig. 5. Since the 10-min sampling time at the rate of 800 l/min corresponds to a sampled volume of 8000 l of air, the preconcentrator could not be applicable to containers of <8000 l. The 4-ng or 5-ng analyte yield from a 10-min sampling time is well above the lower detection limit (LDL) of avail-
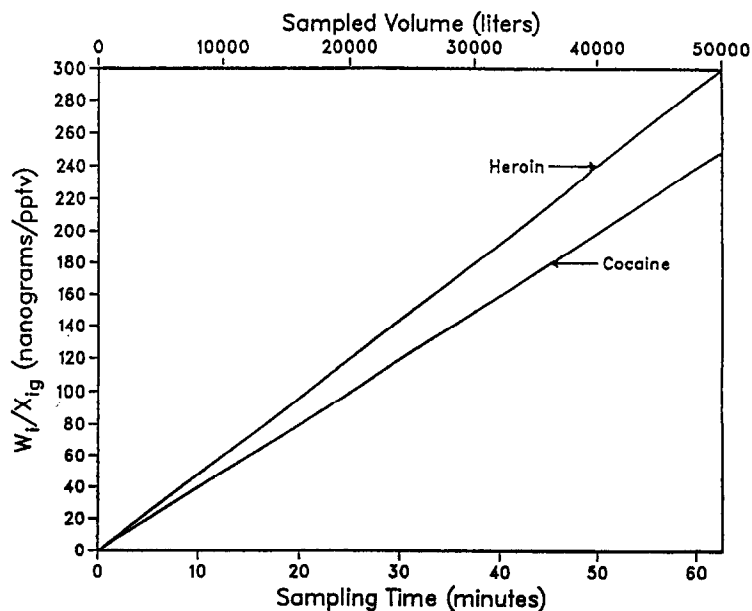

Fig. 5. Dependence of the ratio of collected analyte mass, W_i, to the analyte mole fraction, X_{ig}, on the sampling time or volume of sampled air, assuming a collection efficiency of 40% and an air flow-rate of 800 l/min.

able analyzers. The LDLs of our LC–ED procedures were 0.5 ng for heroin and 2 ng for cocaine.

Adaptability to most analyzers. The analyte-enriched absorbent should require few or no preparatory steps before introduction into most liquid-phase analyzers, such as a liquid chromatograph, a colorimeter, electrochemical systems, or immunoassay detectors. For gas-phase analyzers, such as a gas chromatograph or mass spectrometer, special interfaces may be required. The HTLAP's preferred absorbent drip rate of 0.1–2 ml/min coincides with the liquid flow-rate used in existing LC–MS interfaces [8].

Applicability to many compounds. Comparison with results obtained from various types of liquid-absorption samplers indicate that the HTLAP should be applicable to many analytes of interest, including trinitrotoluene [5], primary aromatic amines [4], nitrogen dioxide [9], hydrogen peroxide [10], formaldehyde [10], sulfur dioxide [10] and several inorganic halogen compounds (HCl, HF, F_2, and other hydrolyzable fluorides) [11].

The HTLAP should be especially useful in detecting and quantitating compounds that are not readily analyzed by conventional preconcentration with GC, *e.g.*, polar or highly reactive analytes, such as primary aromatic amines or hydrazines. Through a proper choice of liquid absorbent it should be possible to achieve high selectivity and/or stabilization of labile or reactive analytes and/or entrapment of volatile analytes. For instance, to trap N_2H_4 vapor, a non-volatile aldehyde may be included in the absorbent. Conversely, to trap formaldehyde, the absorbent may contain a non-volatile hydrazine compound.

CONCLUSIONS

With the collection efficiencies of 40–60% (Fig. 4) and a throughput of 600–700 l/min, the sensitivity enhancement achievable by the HTLAP will depend on the analyte, the analyzer, and the sampling time. For most existing analyzers that operate at sampling rates of <200 ml/min, the HTLAP's much higher throughput will yield a >1000-fold higher rate of analyte collection, with a corresponding increase in sensitivity (reduction in the lower detection limit for the HTLAP-analyzer combination). Alternatively, the required sampling time

could be greatly shortened. Also, with certain portable and fast-responding analyzers, such as ion-selective electrodes, the HTLAP should permit far more rapid on-site air monitoring than was previously practicable.

More work is needed to (a) further optimize the geometry of the preconcentrator tube and the air and liquid flow rates, (b) narrow the range of collection efficiency values under optimized operating conditions and (c) establish the basic design parameters for upscaling or downscaling the HTLAP to higher or lower throughputs.

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