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Dealing with Chemical Risks from Ancient Times to the 21st Century: a Review of Air Sampling and Analysis Techniques

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ABSTRACT

The air sampling and analysis for dealing with chemical risks started in the second half of the 1800s, where a significant role was played by the mining industry relating to dust, carbon mono– and dioxide, and fumes from explosive events. The military industry should be credited with the initiation of exposure control categorization utilizing industrial hygiene (IH) basis with its work. However, despite its relatively long history, air monitoring in IH is still developing. Miniaturization and automation have been increasingly applied in IH during the last ten years, resulting in savings in both time and costs throughout the sampling process. To date, the development of sampling strategies and related devices is constantly evolving: the goal is to develop monitoring systems capable of assessing exposure scenarios in line with the reference limit values, which are constantly being updated downwards. The current situation of air monitoring in IH, concerning analytical instruments, software, devices for performing both personal and environmental sampling are presented. The basics of air contaminants monitoring have been divided into eight topics. The sampling strategies and related devices described are introduced with a historical perspective, from 1873 to date, underlining their continuous evolution. This review aims to represent a useful tool to face different exposure scenarios in IH, showing the most common accessible sampling strategies and the sampling devices available on the market.

KEYWORDS

Chemical risks, industrial hygiene, history air monitoring, air sample collection.

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1. Introduction

Human hazard assessment has a fundamental aspect in the evaluation of human exposure to toxic and genotoxic contaminants. Generally, appraisal of the risk of xenobiotics is founded on the determinations of their concentrations by the analytical chemistry and their toxicity and genotoxicity data. To obtain protection against the deleterious effects of pollutants, an

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accurate determination of their levels is required. Therefore, the execution of many samplings (daily, monthly, or yearly time-weighted) to estimate the average quantity of harmful contaminants must be carried out to determine the quality of living areas and workplaces. Moreover, this approach could be used to mitigate the risk because it helps to find and focus on harmful situations and so, prevention measurements can be taken.

The effects of chemicals on human health were noted more than 21 centuries ago.[1] Already during the Roman time, Marcus Vitruvius Pollio indicated the presence of illness in workers who were exposed to lead in the manufacturing of water tubes ('*De Architectura*, Book VII') and Gaius Plinius Secundus reported that sheep bladders were used as masks by workers to protect themselves from lead and dust when working with lead carbonate or mercuric sulfide in the production of dishes.[2] In Europe, in the 11th and 12th centuries, the mining industries were growing and the exposure risk of workers in mining and smelting of metals became well-known. Thus, to help sick workers guilds were created: one of the first was founded in Germany in 1188 among the silver miners of Goslar. In 1556, 'black lungs' in miners and hazards related to mining and smelting of metals were reported in *De re Metallica* by Georg Agricola.[3] In 1713, *De Morbis Artificium Diatribe* by Bernardino Ramazzini was the first treatise on working related diseases and industrial hygiene (IH).[4] It reported the health risk of irritating chemicals, dust, metals and other agents that workers can come in touch with, in several occupational scenarios; furthermore, Ramazzini outlined growing interest about miners in different European areas. At the beginning of the 20th century, the Factory and Workshop Act was emanated in Britain to safeguard the industry's workers that were exposed to rough and grimy conditions.[5] More recently, the Control of Substances Hazardous to Health (COSHH) was founded and in 1988, it persuaded industry to increase the consideration of their responsibilities to the employers.[6] Following COSHH recommendations meant evaluating the risk to workers and this would mean finding a way of monitoring exposures.

Today, around 2.8 million workers per year globally die from unsafe or unhealthy work conditions.[7] From a World Health Organization report, approximately 355 000 people globally are killed by unintentional poisonings.[8] In industrially developing countries – where most of these deaths occur – these kinds of poisoning are strongly related to exposure and incorrect use of chemicals.[9]

Monitoring air quality is an essential part of health and safety. Air sampling is a way to investigate and control air composition as a function of time. Different strategies can be used to perform air sampling. Each strategy has advantages and disadvantages, and the best choice depends on a combination of available resources, the necessary application and the potential health risks posed by the workplace.

The South African school can be considered pioneering in the use of air sampling devices. James Moir[10] (Fig. 1) can be seen as the pioneer and Sir Robert Kotze[11] moved on to relevant developments. These approaches to assess the exposure were characterized by different expectations for air sampling from the industrial hygienists; moreover, they had different orientations for evaluating the results. Before the late 1970s, the activity today known as exposure assessment was not seriously established and structured.[12] To understand the idea of workplace quality assessment today, you need to know the methodologies and theory that were the basis of air sampling in the early years of its history. The concept of exposition at that time was linked only to short-term exhibition phenomena, to which a short-term sampling system refers.[13,14] Nowadays, a wide range of methods and devices are available to be used for sampling and to perform analysis of pollutants that may be present in any environment. For example, appropriately characterizing individual spatio-temporal mobility are recently developed in air sampling[15] by detailed activity diaries,[16] GPS devices[17] or smartphone-based location tracking applications[18] to record individual human movements.


Figure 1 James Moir. [10]

The modern IH protocols use the analytical proficiency testing (PAT) to indicate the level of agreement among laboratories analyzing workplace environmental samples, as well as the number of laboratories performing those analyses to improve the accuracy and reproducibility of these results.[19] Therefore, the development of laboratory information management systems (LIMS) began with the need to manage laboratory samples, the analysis associated with them and related reports to save time during processes.[20]

This review article points out the historical approaches and methodologies to measure airborne concentrations of chemical contaminants utilized in the world from its origin in 1873, the year in which the Orsat analyzer was patented,[21] until today. In particular, we show the development of the air monitoring from 1904, with the early air-samples analyses dealt by James Moir,[21] to 1973, when Palmes proposed a diffusive air sampler.[22] We consider this time frame as the period that includes the fascinating development of primary and essential samplers and instruments for gaseous and particulate matter analysis. Despite its relatively long history, air monitoring in IH is still under development, introducing the miniaturization of samplers with new geometries, the measurement of nanoparticles, the sophisticated field instrumentations, as well as the smart portable detectors for continuous, direct reading and their remote management, ensuring the accuracy and reproducibility of results through Quality Assurance programs. In our work, eight topics, considered fundamental for the IH, are analyzed from a historical point of view, presenting their origins and their evolution up to the current date. Furthermore, the present-day state of the art of each monitoring devices, selected in this review, is presented, showing the commercially available alternative on the market. This approach could represent a useful tool to face different IH questions and contexts.

2. Air Sample Collection

Proper air volume collection can be considered crucial to acquire significant analytical results. Generally, to sample adequate air volume, sorbent samplers required an 'active sampling' using a manual or electric pump: a small pump with low flow rates (10 to 200 mL min^{-1}) is the most used system to collect air sample on sorbent; when samples of high volume are required, cartridges with a larger volume of sorbent phase can be used. Nowadays, to obtain robust and sensible results, the tendency is to enlarge the volume of the air sample. We look at some of the key moments in history behind sorbents and sorbent air sampling devices.

2.1. The First Sampler to Collect Air: the Impinger by Absorption

The Greenburg-Smith impinger and the midget impinger, developed in 1922[23] and 1928 by the US Bureau of Mines (USBM), in collaboration with the US Public Health Service, and the American Society of Heating and Ventilating Engineers[24] and the USBM, respectively, collected particles bigger than about ¾ micron in a liquid phase. The quantitation of collected particles was carried out by counting all the particles that sink to the bottom of the counting cell, using a ×10 magnification lens. The Threshold Limit Values (TLVs) for mineral dust and 'nuisance' particulates used by the TLV-Committee of the American Conference of Governmental Industrial Hygienists (ACGIH) were based on particles ft^{-3} by impinger air sampling counted with light field techniques.

The large Greenburg-Smith and Hatch impingers were ideated with a 2.3 mm nozzle to sample air at a rate of 1 cfm at a nozzle velocity of 100 m s^{-1}.[23] The collection was carried out in 75 to 100 mL of sampling medium.[23] A modification of the large impinger, the midget impinger, was designed for a more straightforward utilization. There were two main varieties: i) Bureau of Mines impinger with an airflow of 2.8 L min^{-1} at a pressure drop of about 30 cm of water and a nozzle velocity about 60 m s^{-1} (samples are collected in 10 mL of liquid), and ii) Wilson impinger with a rate of 5 L min^{-1} at a pressure drop of about 50 cm of water. The nozzle velocity was about 100 m s^{-1} (same as the large impinger). The higher nozzle velocity provided a greater collection efficiency for fine particulate matter.[25]

All glass midget impingers are available in both modifications with Teflon baffles[26] and with impingement plates attached to the jet. These must be used when rubber dissolved from the stopper will interfere with the chemical analysis, or when an ultraviolet or infrared adsorption method is needed. The high cost of all-glass impingers prevented the exclusive use of this type of samplers. Since the midget impinger is more convenient to use, it has widely replaced the bulky large impinger for fieldwork. Moreover, the development of more sensitive chemical methods has dwindled the need to sample the larger volumes of air, that is collected with the large impingers. This is true when sensitive analytical techniques are used.

In 1965, A. Linch and M. Corn presented an optimization of classic midget impinger, the micro-impinger, which needs less liquid phase, as a sampling medium (2–3 mL).[27] This model was endowed with a flexible O-ring joint, instead of the ring seal, to support the impinger tube. This introduction reduced the fragility of the device and allowed lateral setting of the sampling orifice distance; moreover, this provided interchangeable orifice.

These samplers are quite cheap, and they can be interchanged easily, allowing customization by selecting orifices with pressure drop-flow rate tolerance, making individual calibration needless. The international market offers impingers in Pyrex® glass or fluoropolymer to meet many applications in different fields, as environmental[28] or occupational[29] monitoring, as well as impinger holsters and holders for greater strength.

2.2. 1935. To Retain the Air More Easily: Adsorption by Solid Sorbent

Solid adsorption is one of the most useful and commonly employed preconcentration strategies to evaluate volatile trace pollutants that are present in the environment and the workplace.[30] The trap, that retains the compounds that have to be analyzed in an exact air volume, is commonly made of glass or metal tubing. Both thermal desorption and solvent extraction are possible to perform the desorption step.[31] The adsorbent material is crucial, so its choice is fundamental and needs to be based on a good knowledge of its properties.[32]

In 1935 the *Journal of Industrial Hygiene*[33] published benzene collection methods (Fig. 2A), where materials like activated charcoal and silica gel allowed the retainment of vapours efficiently. However, the release of the collected vapours was complicated. The benzene was frozen from the air onto glass beads; then, it was released by increasing the temperature. Then, in 1936, tubes filled with dried charcoal (Fig. 2B) were described in the *Journal of Industrial Hygiene and Toxicology*;[34] they were analyzed through pre- and post-weighing. How to desorb and analyze single contaminants through the gas chromatographic system, after collection on activated charcoal, was described by the ACGIH in 1964.[35] This method is nowadays the basis for most of the current sorbent sampling, while the range of methods is varied and adapted to the contaminant. On 17 April 1972, the National Institute of Occupational Health & Safety (NIOSH) proposed the first method using charcoal tubes: it set parameters for measuring benzene and a measuring range, a detection limit and a percentage accuracy.[35] So, NIOSH approached Lloyd Guild on an application using tubes and in 1973, Scientific Kit Corporation – officially became SKC Inc. in 1979 – manufactures 6000 commercial tubes with two sections of the sorbent. In 1982, SKC Limited established a European and an Africa head office in the United Kingdom and South Africa, respectively. In 2012, SKC Asia was established in Singapore. Today SKC Inc (Pennsylvania, USA) is one of the world leaders in sampling products for Industrial Hygiene (IH).

At the end of 1980, Kaiser[36] proposed the porous spherical carbon molecular sieves, called Carboxen™ and Carbosieve™ by Supelco Inc. (Pennsylvania, USA), and Spherocarb® from Analabs Inc. (Colorado, USA).[37] Non-porous graphitized carbon blacks (Carbopack™ and Carbotrap™ by Supelco Inc.) made its appearance a few years later. Other typical adsorbents for air sampling are the polymers Tenax® by Akzo and now, trademark Buchem BV (Apeldoorn, Netherlands), PoraPak™ by Waters Corporation (Massachusetts, USA), Chromosorb® (thanks to Johns Manville and Imerys Minerals California, Inc. USA), HayeSep® (Hayes Separations, Texas, USA), silica gel (Rhone Poulenc/IBF), and molecular sieves (zeolites) by Union Carbide Corporation (Texas, USA).[38]

More recently, solid sorbents are most often tube-type devices included chemical colour-comparison gas detector tubes. They are thin glass tubes with calibration scales printed on them, to

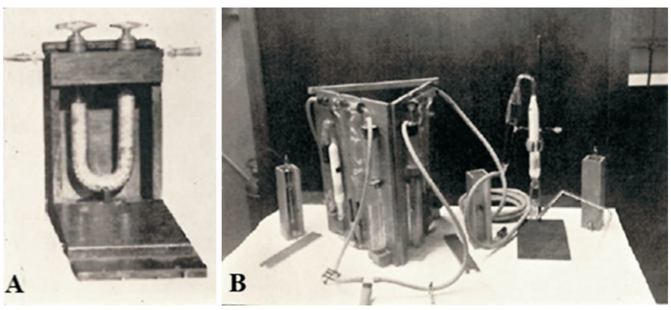

Figure 2 (**A**) The first activated charcoal and silica gel tube for benzene vapour. [33] (**B**) Activated charcoal apparatus used for field determination.[34]

read the concentration of gases and vapours that must be measured. These devices are marketed by Gastec Corporation (Kanagawa, Japan), Uniphos and KwikDraw (Uniphos Envirotronic Pvt Ltd, Gujarat, India), Kitagawa (Komyo Rikagaku Kogyo KK, Kanagawa, Japan), and Dräger (Dräger Inc., Texas, USA). Alternatively, other geometries are represented by LpDNPH cartridges and ORBO tubes (Supelco Inc., Pennsylvania, USA), OSHA Versatile Sampler Tubes (SKC Inc., Pennsylvania, USA),[39] and Sep-Pak® cartridges by Waters Corporation (Massachusetts, USA), up to active solid-phase microextraction techniques represented by NeedlEx (Shinwa Chemical Industries Ltd., Kyoto, Japan), SnifProbe (Aviv Analytical LTD, Hod Hasharon, Israel), MEPS (SGE, Trajan Scientific Australia Pty Ltd, Australia), and μSPEed® (ePrep Pty Ltd, Victoria, Australia) (Fig. 3). COGNI™ System is an innovative tube for labelling, identification and tracking system from Camsco® (Mayard, Texas, USA). The latter is a manufacturer of absorbent tubes for the American army, since 1991, and it was the first laser-marking facility high-temperature ceramic decals for ensuring tubes identification and tracking. In 2008, Camsco® promoted its brand outside the military and intelligence communities.[40]

2.3. A Few Years Later the Vapour Phase was Separated from the Dust Particle

Semi-volatile organic compounds, due to their physiochemical characteristics, can be in the air as free gaseous molecules, but furthermore, they can be found as chemical compounds adsorbed onto dust particles. To allow the sampling and the separation of these two different phases of semi-volatile organic pollutants in an air sample, a diffusion denuder can be employed: vapour and particle present different diffusivities through the denuder, thus, first, the vapour phase is collected on a sorptive surface, then the particulate phase goes through the device and it is gathered on a downstream filter.[41]

2.3.1. *Denuder*

The first theoretical approach with the denuder tube dates back to the 1890s, during a study about the diffusion of ions into gases.[42] In the 1930s Zulfiqur *et al.*[43] indicated in studies of atmospheric condensation nuclei that gas flowing through pipelines presented particulate losses and this brought the diffusional removal of particulates in pipelines into consideration.[43] Several studies of the diffusional properties of particulates were carried out with multi-tubular assemblies and diffusion batteries. Studies concerning the diffusional analysis using these approaches continued, and in 1949 Gormley and Kennedy[44] described diffusion of a vapour flowing through a cylindrical tube, firstly proposed by Townsend.[42] In this experiment, Gormley and Kennedy incorporated laminar flow subduction zones incorporated at the inlet to these tools, and the sulfur trioxide and ammonia diffusion coefficients were obtained by measuring the mixing ratios of these gases within the piping. Zulfiqur *et al.*[43] reported in the early 1960s, that a study concerning the effects of fluorides in the atmosphere was done; in this experiment, an annular unit was used to separate free airborne fluoride from their particulate phase, using three concentric cylinders coated with sodium hydrogen carbonate or aluminium. Subsequently, an analytical technique using an

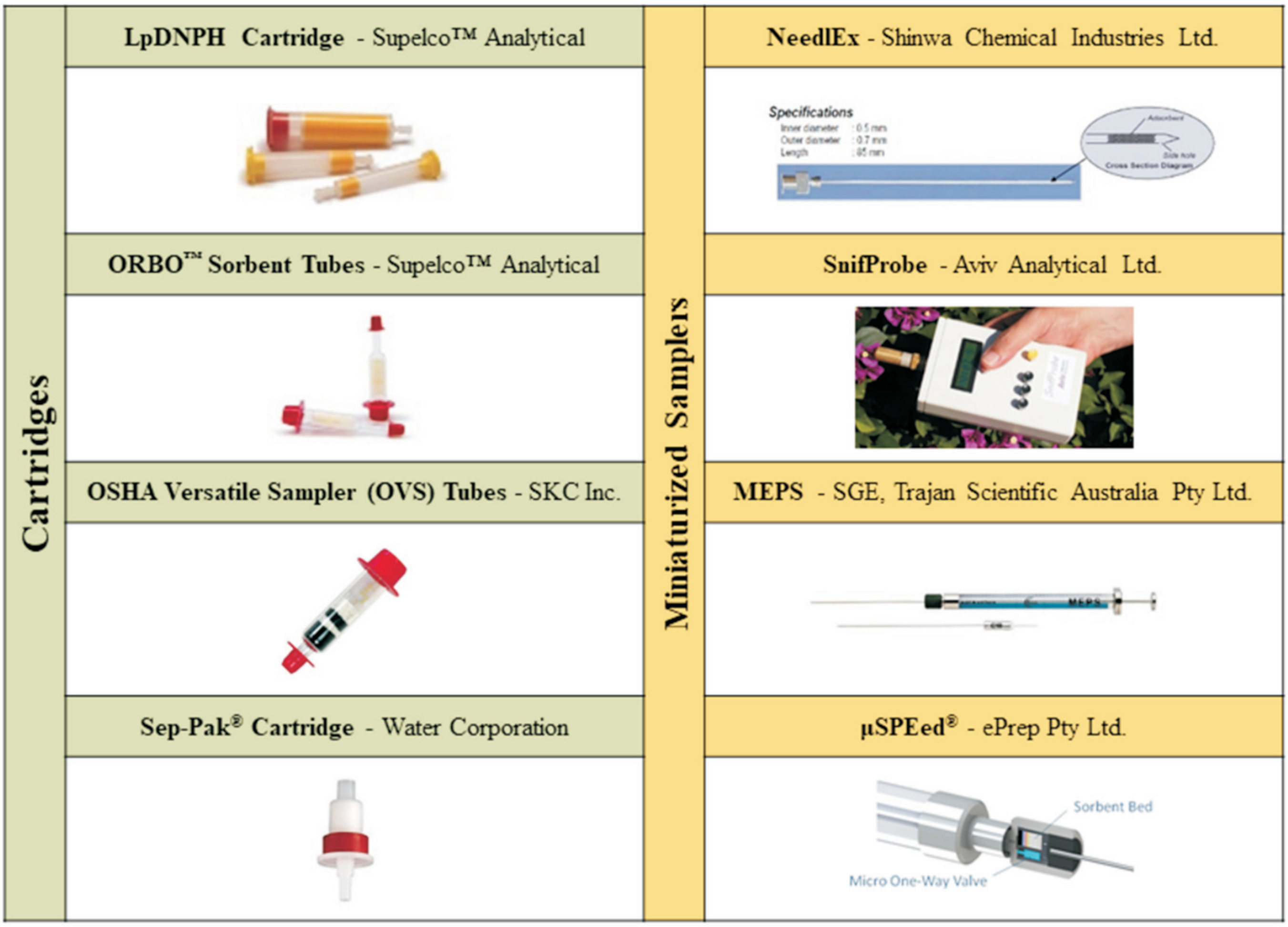

Figure 3 Commercially available cartridges and miniaturized needles for active sampling.

'aerosol-passing gas adsorber' was described: this device was used to reduce the influence of water vapour on a hydrogen flame chemiluminescence aerosol sampling system and it was done by aligning in series of glass tubes with potassium hydroxide and magnesium perchlorate. The removal of sulfur dioxide from a laminar flowing gas by a denuder coated with lead(1V) oxide was carried out to comply with the Gormley-Kennedy equation.[44] The introduction of heating the sample tube to produce thermochemical variations in ammonium sulphate samples was first showed in 1978. The use of a set of aligned denuder systems allowed higher gas flowrates, and it was used in environmental sampling to remove ammonia and other gasses from air samples. However, until 1979 the denuder tube was used only as a gas sampling device instead of a tool to denude particle samples of specific gaseous components.

Nowadays, conventional solvent-extracted diffusion denuders commercially available include annular, multi-channel, coiled, Terkan quartz, multi capillary (URG Corporation, North Carolina, USA), ASSET® EZ4 Dry Samplers (Supelco Inc., Pennsylvania, USA) and honeycomb (Thermo Fisher Scientific, Massachusetts, USA), also designs with adsorbents, such as Tenax or Florisil. Recently, denuders were thermally desorbed in commercial thermal desorption stations for subsequent analyses. Ortner and Rohwer[45] originally developed a polydimethylsiloxane multi-channel trap for the analysis of semi-volatile air pollutants and van Vuuren and Naudé[46] in 2019 introduced an air sampling tool, consisting of a standard GC inlet liner that can be compared to a mini-denuder (Fig. 4).

2.3.2. *Particulate Matter Sampling*

During the period from 1860 to 1880, researchers could for the first time collect particles from the air, inspect and study them under a microscope; this was thanks to impactors.[47] For the next 25 years, very few impactors were developed. Then there was a surge of impaction instrument development to study industrial aerosols, particularly in mines. Already in the early 1900s, materials like the crystalline silica or quartz particles were recognized as dangerous; in fact, they led to the miner's phthisis, which is a lung disease.[21] Due to this, methods to test dust in mines were developed; in this process of development James Moir played a leading role.[10,48–50] Back then, there were two ways to analyze the dust in mines: the first method was a gravimetric one, using a sugar tube, while the second one was the konimeter.

In the beginning, the gravimetric sampling was led by South Africa, followed by the UK and then by the USA. To perform the sampling, a known volume of air was passed through a tube, within which there was a filter media. At first cotton-wool fibres were used as filter media; the mass of the dust particles sampled was determined by weighing the cotton-wool fibres before and after the sampling. Sometimes the cotton plug was burned and then the residue was weighed. Around 1903 some determinations of dust were performed by using a tube filled with a packed bed of sugar granules as a filter medium. The mass of the insoluble material collected on the filter medium was determined after the dissolution of the sugar granules in water – James Moir was especially involved in the development of this technique. Particles collected with this technique could be observed or even analyzed utilizing a microscope. In Gray's later reports,[51] the

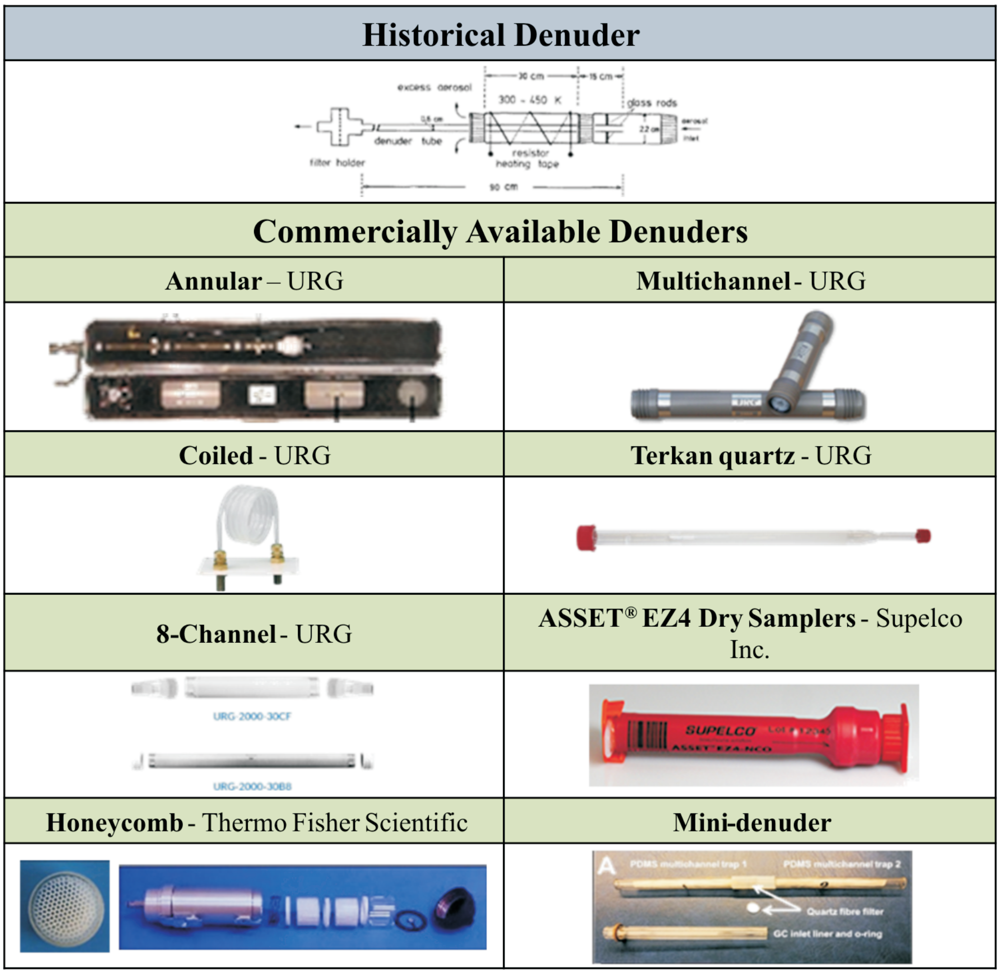

Figure 4 Types of denuders.

action mechanism within the sugar cube was described. In essence, the grains of sugar constituting the filter medium were too large, in comparison with the dust particles, so they could not operate as a filter to catch the dust; the air needed to pass-through grains of sugar that were lightly moist. The result was merely given by the impacts of the particles in the air passing through the sugar cube. The time between 1920 and 1945 was characterized by development, which consisted primarily of the refinement of three devices developed around 1920. In 1945 the subsequent development of the May cascade impactor happened;[52] it furnished information regarding particle size distribution and their concentrations. This development on dust in air sampling was related to military studies on chemical dispersion on the battlefield. Many impactors were developed following the cascade impactor of 1945;[53] a lot of them were variations of the original one, namely the May cascade impactor. During the same period, serious work began to understand fluid and particle movement in impactors by theoretical analysis. First was the Mining Research Establishment (MRE) gravimetric sampler, developed by Dunmore *et al*.[54] The respirable dust particles passed through the elutriator and were then collected on a filter for weighing. A personal sampler was developed for mining use, driven by USA Atomic Energy Commission research[55], which found that dust particles larger than 7 μm could be removed by a commercially available 10-mm nylon cyclone.

During 1970, the employment of high-speed computers and finite difference methods allowed an accurate understanding of the flow and the particles' trajectories inside impactors. The theoretical work obtained in that period showed, if specific guidelines were followed, how impactors could provide accurate particle size classifications with predicable aerodynamic cut-off sizes. Thus, in 1970 the design of impactors entered a new era with Lovelace Low Flow Rate Impactor,[56] Pilat (UW) Stack Impactor,[57] and the quartz crystal microbalance (QCM) cascade impactor (California Measurements, Inc., California, USA).[58]

Fifty years later, cascade impactors are still widely used to measure aerosol mass size distribution and to collect samples to perform chemical analysis.[59] Nowadays, the increasing interest in the nanoparticle has led to the development of cascade impactor, characterized by the inclusion of cut-off aerodynamic diameter covering the nano-size range: the micro-orifice uniform deposit impactor (MOUDI),[60] the electric low-pressure impactor (ELPI), and NCTU micro-orifice cascade impactor (NMCI) developed and tested to avoid possible particle clogging in the nozzles using new nozzle plates with smooth nozzle shape of 120 mm in thickness.[61]

2.4. Air Samples are Collected and Stored in Plastic Bags

The modern IH approach to air sampling looks at cheap, portable and easy to use sampling containers and these requirements are fulfilled by the sealed plastic bags with air valves. These containers have been used since the 1940s and today, different kinds of sampling bags are commercially available, and they can be employed in several analytical, environmental, occupational scenarios according to specific compounds.

Measurements of gas diffusions through plastic film[62–64] were performed from 1947. Wilson and Buchberg observed[65] that Kel-F (manufactured by Minnesota Mining and Manufacturing Company, Minnesota, USA) was suitable for sampling airborne nitrogen dioxide, acetone, pentane, cyclohexene and methane.

Plastic bags have been largely employed to evaluate human exposure to air contaminants and toxic gasses.[65] In 1964, Conner and Nader showed the application of a technique, where the plastic bag was put inside a rigid container and inflated by creating a vacuum between the walls of the containers and the bag.[66–78]

Recently, the market has proposed ALTEF gas sampling bags, made from a polyvinylidene fluoride (PVDF) film and Multi-Layer Foil, a protective four-layer barrier, minimizes gas permeability: nylon (outer layer), polyethylene, aluminium foil, and polyethylene (inner layer) (Table 1).

2.5. 1980. Stainless Steel Enters in Industrial Hygiene: the Canister

The canister sampler is a spherical or cylindrical stainless steel (ss) vessel – with volume ranging from 1 L to 6 L – ideated to hold

Table 1 Historical development of sampling bags.

Reference	Year	Material
Wilson and Buchberg	1958	Kel-F
Baker and Doerr Scotchpack	1959	Mylar, Aluminized Mylar, Saran. Scotchpack and Aluminized
Boettner and Dallos	1959	Saran
Altshuller *et al.*	1962	Scotchpack and Mylar
Ringold *et al.*	1962	Polyvinal chloride
Stewart *et al.*	1962	Saran
Altshuller *et al.*	1964	Mylar and Rubber
Conner and Nader	1964	Mylar and Teflon
Clemens and Altshuller	1964	Mylar
Confer and Brief	1965	Mylar
Vanderkolk and Van Farowe	1965	Mylar
Schuette	–	Aluminized Scotchpack
Tamplin	–	Aluminized Scotchpack
E.I. du Pont de Nemours and Company (Washington USA)	1971	Tedlar®
Adtech Polymer Engineering Ltd (England,UK)	1999	PFA, ETFE, CTFE, ECTFE. PVF
Restek Corporation (Bellefonte, USA	2013	ALTEF
Ghimenti *et al.*	2015	Nalophan™, Tedlar® and Cali-5-Bond™

Perfluoroalkoxy (PFA), Fluorinated Ethylene Propylene (FEP), Ethylene Tetrafluoroethylene (ETFE), Chlorotrifluoroethylene (CTFE), Ethylene Chlorotrifluoroethylene (ECTFE).

vacuum to less than 10 mTorr or pressure to 40 psi. Sampling with the canister can be performed by simply opening the sampler and the vacuum inside the canister draws in a sample within a matter of seconds (e.g. odour events or static concentration streams) or by using a flow controller to collect the sample over a specific time frame or at a given flow rate. After the conclusion of air sampling, the canister opening is re-sealed, generally, with a brass bolt and the sampler can be brought in the laboratory to be analyzed.

The canister technique was developed during the 1980s by the Environmental Protection Agency (EPA)'s Air Monitoring Center in Research Triangle Park. The initial development of ss canisters was carried out by the study group of Rasmussen at Washington State University, that first applied this kind of sampling device to collect air samples:[79] the goal of the study was to evaluate background concentration of trace gases and their long-term concentration trends. Mc Glenny *et al.*[77] reported that several members of the Rasmussen group, including the co-author M.W. Holdren, continued their projects with canister-based protocols, either in their application to air sampling or by the commercialization of the associated hardware.[79] The canisters were produced by several manufacturers, such as Scientific Instrumentation Specialists (Moscow, Russian), Biospherics Research Corp. (Biospherics Research Corp., Oregon, USA), Andersen Samplers Inc. (Andersen Samplers Inc., Georgia, USA). The canisters were made of 304 ss; the inlet was a Nupro SS-4H (Nupro Company, Ohio, USA) metal bellows valve with a non-contaminating valve seat material. Two types of canisters are available, differing by their interior surfaces: the SUMMA® canister's internal surfaces are passivated using a Molectrics Summa Processing (Molectrics, Inc., Ohio, USA) and the new canister generation is typified by the SilcoCan™ (Restek, Pennsylvania, USA). The SilcoCan™ is made of ss, and its inner layer is electropolished, and an inert layer is chemically bonded to the interior surface.

Recently, Australian Laboratory Services (ALS, Utah, USA)proposed Helium Diffusion Sampling (HDS):[80] using helium diffusion technology, an air sample is collected by making a vacuum that actively retrieves air in as helium goes out. Before each sampling, every HDS monitor is vacuum-cleaned and pressurized. The helium also contains bromofluorotoluene (BFT) as an internal standard to confirm leak-free operation and ensure the robustness of every sampler by monitoring BFT recovery.

3. Personal and Area Air Sampling Pumps

The first personal monitoring air sampler was developed by the US Bureau of Mines in 1937 for dust sampling by coal mine workers using impingers connected to a manual pump[81] (Fig. 5A), hand-operated by a second person. In 1957 the first battery (Fig. 5B) operated personal pumps were used, made under contract for the US Bureau of Mines; samples were collected onto filters, using size-selective cyclones. In 1962 a commercial pump was first sold in the USA and Europe; in 1973 a low flow pump for sorbent tubes was proposed, while the constant flow pumps were only available in 1975. More recently, in 2011 Spectrex Corp. (California, USA) proposed PAS-500 Micro Air Sampler with a drastic reduction of weight (114 g) and size (30 × 20 × 109 mm), when compared to the traditionally low volume pumps; moreover, one of the best advantages of this model is the holding-pump clip, that tightly holds the devices without requiring a long hose.

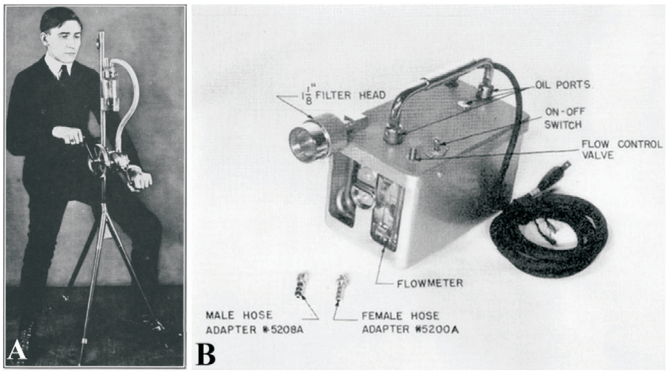

Figure 5 (**A**) Manual pump.[81] (**B**) The first pump working with battery.[82]

Concentrations of several pollutants are known to change spatiotemporally, thus, operator mobility could reflect in uncertainty in exposure assessment, consequently leading to exposure evaluation errors that can lead to biases in statistical analyses. Recently, Sensidyne (Florida, USA) introduced GilAir® Plus personal air sampling pump with Bluetooth connectivity, mobile app and motion detection, which could help to overcome spatiotemporal pollutants variations.

Concerning environmental pollution assessment, many companies are already offering portable sequential sampling devices, with remote management *via* GSM or Wi-Fi, to collect gasses, vapours and particulate matter, using tubes, filters, denuders, canisters, and/or bags. Designed to comply with Environmental Protection Agency speciation requirements, the portable sequential sampling devices more and more frequently are used in IH for area sampling.[83] In 2018 AMS Analitica (Pesaro, Italy) proposed a 12-position sorbent tube sequential called GasCheck™. To date, other sequential sampling devices are CEH DELT® System (Centre for Ecology & Hydrology, Penicuik, UK), SASS™ speciation sampler (Met One Instruments Inc., Grants Pass, OR, US), URG-2000 (Chapel Hill, NC 27516 USA), Partisol® Model 2300 Sequential Speciation Sampler (Thermo Fisher Scientific, Massachusetts, USA), and GAS08/16 (Envint, Montopoli di Sabina, Italy).

4. 1973. The First Passive Sampler by Palmes

During the past 30 years, the technology of passive sampling has developed and improved very fast. Thanks to many meaningful advantages, such as easiness, low cost, no need for expensive or complicated equipment, no need for power, unattended operation, silent operation and the capability to provide accurate results, it is widely used to monitor pollutants. This kind of sampling is vital, especially for multipoint sampling. The physical principle on which passive sampling is based is the diffusional mass transfer that occurs through a static layer of the sampled medium and a membrane, as described by the first law of diffusion of Fick.[84] It dates back to 1927, the first time that a diffusive sampler[85] was applied to carry out a semi-quantitative determination of carbon monoxide. Palmes introduced a truly quantitative open tube diffusion sampler in 1973 for the determination of NO_2[86] and SO_2[87] in the air (Fig. 6). Frequently, diffusive

Figure 6 Palmes tube diffusion sampler.[22]

samplers are tube-type devices and their highest expression are Passam[88] and DSD[89] marketed by Passam Ag (Mannedorf, Switzerland) and Supelco Inc., respectively. Badge-type diffusion samplers are also used. They were introduced in 1986 from National Institute of Working Life in Umea, Sweden, in collaboration with SKC Inc. The UMEx Passive Sampler paved the way to Ogawa Passive, ACS Vapor Monitor (Advance Chemical Sensor, Florida, USA) and Analyst; in this kind of devices, the diffusion barrier is usually a layer of a microporous material, that separates the collecting medium from the outside air.

In the mid-1990s the director of the Fondazione Salvatore Maugeri in Padova, Vincenzo Cocheo, in collaboration with the European Commission's Joint Research Center, developed and patented a diffusive/sampling design that proved to be revolutionary. A radial symmetry device registered with the Radiello™ trademark:[90] a radial diffusive body of porous polypropylene with an adsorbent cartridge positioned within. Thanks to the symmetry, an increased uptake rate can be achieved; in fact, analytes can penetrate the adsorbent material throughout the 360 ° surrounding diffusive body. Based on the same principles, Acquaria (Acquaria s.r.l., Milano, Italy) developed RING, a radial symmetry sampling device with an increased thickness and, therefore, higher load capacity, which allows greater linearity on long-term sampling.

Recently, passive solid-phase microextraction techniques namely SPME® by Supelco Inc.,[41,84,91,92] Thin Film (TF)-SPME (Gerstel, Mülheim an der Ruhr, Deutschland), Twister® (Gerstel, Mülheim an der Ruhr, Deutschland),[93] HiSorb (Markes International, Sacramento), MonoTrap™ (GL Sciences Inc., Tokyo, Japan), and Sorbent Pens™ (Entech Instruments, California, USA) have been proposed as interesting alternatives to conventional diffusive passive samplers (Fig. 7).

5. The Post-sampling Phase: Analysis and Related Automation

Based on various estimates, sampling and sample preparation usually represent 70–90 % of analysis times. Because of that, it is evident that often the most significant income in the overall response time of the analytical system can be obtained with the reduction of the necessary time to process the samples. Liquid chromatography (LC) and GC equipped with a flame ionization detector (FID) and mass spectrometry (MS) have been used to perform most of the analysis on sorbent samplings. Automation and the adoption of robotic arms coupled with this kind of instruments can be used to achieve a shorter time of sample preparation and analysis. They are usually classified according to the configuration or their geometric coordinate system. The most common ones are Cartesian (or rectangular), polar (or spherical), cylindrical and revolute (or anthropomorphic). With this type of robotic arms, at least three degrees of freedom are allowed. The fact that the robotic arm can change tools does not require continuous supervision and activities of an operator, even if the process is multistep, this significantly increases the productivity of laboratories. Simultaneously, the safety of the process is optimized by the traceability of all operations. Transferring error-prone manual tasks to a robot improve robustness. During the last ten years, there has been a proliferation of the on-line XYZ autosamplers; this has contributed to the increase of the practice of hyphenated techniques in analytical chemistry. The first company to offer a commercial three-axis autosampler for gas-chromatography was CTC Analytics AG (Zwingen, Switzerland). In 1986, A200S was the first GC liquid autosampler released on the market. In 1998 CTC Analytics produced the PAL system platform, which then, in 2003, was extended into the HTX PAL by creating an extended x-range; between 2012 and 2014, it has presented its PAL RTC, RSI, and LSI systems. Leap Technology Inc. (Trajan Scientific and Medical, Ringwood Victoria, Australia), Chromtech Analytical Instruments (Bad Camberg, Germany), Gerstel GmbH & Co. KG (Mülheim an der Ruhr, Germany), Da Vinci Laboratory Solution BV (Rotterdam, the Netherlands), Anatune Ltd. (Cambridge, United Kingdom) and Axel Semrau (Sprockhövel, Germany) currently produce other on-line automation solutions front-end. These autosamplers can perform the sample preparation thoroughly; in fact, they are equipped with all the necessary tools. So, they can have, for example, a robotic tool change, a bottom sensing, a vortex mixer, the centrifugation, the weighed with balance; through all the process, the traceability is given by a barcode reader. Some companies, like ROBOKROM (KONIK Group, Barcelona, Spain), FLEX (EST Analytical, Fairfield, USA), Primariz (Moduvision Technologies, Vlissingen, Netherlands) and CONCEPT MIS (PAS Technology, Magdala, Germany) have recently introduced new XYZ autosamplers on the market. The HT2800T is a next-generation autosampler characterized by two-axis; it was recently produced by HTA (Brescia, Italy). Among the most performing and versatile devices to do air sampling, there are SPME®, Twister®, and MonoTrap™.[94–97] For these solid-phase microextraction techniques, the need for high-throughput analytical sessions requires specialized systems. As a result, the following systems were developed, FLEX/Multi-Fiber eXchange (EST, Ohio, USA) for SPME® fibres and Thermal Desorption Unit tray (Gerstel GmbH, Mülheim an der Ruhr, Germany) for Twister® and MonoTrap™.[98] The Zymate by Zymark Corp. was the best known cylindrical robotic arm: it is composed of a cylindrical coordinate arm, that has interchangeable hands and various workstations interfaced with a custom controller. Zymark brand and product lines had been acquired by SOTAX AG (Aesch, Switzerland) from Caliper Life Sciences (now part of PerkinElmer) in 2008. In 2014 the remaining Zymark product lines had been rebranded to SOTAX AG, i.e. models like APW and TPW. Two robotic arms have recently been introduced into the market. The first one is the ChromBot (Chromtech Analytical Instruments), which is a laboratory revolute robot that can orientate itself in both dimensions, furthermore in the speed of movement on the human arm (the load capacity is up to 500 g). The second one is the Andrew system (Andrew Alliance S.A., Vernier, Switzerland), which is an automated polar robot that can handle liquid, using Gilson pipettes, and that can be used for several applications. The Thermo Scientific F5 (Thermo Fisher) is a six-axis anthropomorphic revolute robot that has been designed to automate the laboratories. This device is characterized by ±0.02 mm repeatability at full and 5 kg payload. Moreover, Sartorius AG has proposed a robotic system, AF-WEIGH, to weight filters; Da Vinci Laboratory Solution has introduced DryLab, which can be used to develop a chromatography method and to optimize the software. It can predict chromatograms in a very wide range of experimental conditions.

6. Field Instruments

The primary technique to assess workplace pollution throughout the 1904–1973 period, has been based on direct reading chemical reaction media, either chemically impregnated papers or porous media; longer sampling time (minutes) devices instead used direct reading colorimetric liquid reagents. Nowadays, the development of valid sampling and sample preparation processes, with easy operation and ready to use devices, represent a growing field of research. One of the research targets

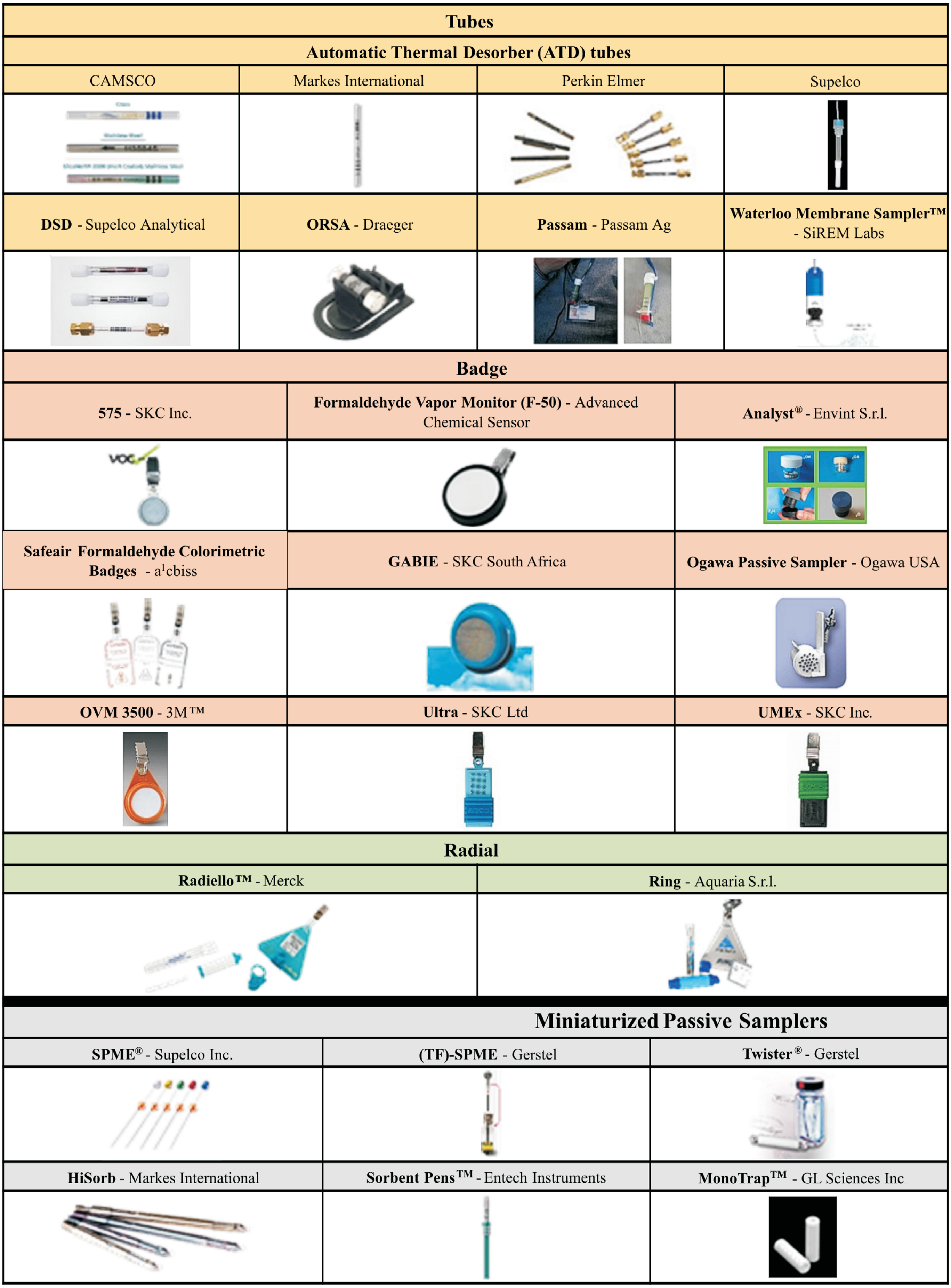

Figure 7 Commercially available geometries passive samplers.

is to combine different steps, like sampling, sample preparation and analysis into one. A fundamental aspect considered in the developments of this kind of procedure is the maximum possible reduction of solvents; this goal could allow a lower cost of the analysis, a reduction of time and labour needed, and solventless techniques have often proven themselves more sensitive that the 'classic' ones. Moreover, the solventless methods are one of the priorities of 'green analytical chemistry', which is rapidly gaining interest in the scientific community.

Direct-reading portable gas monitors (DRPGMs) are firstly applied to monitor the airborne pollutants, which can be found as gases, vapours, aerosols or fumes in the atmosphere. The term DRPGM was introduced in the 1970s to identify those detector tubes whereby the gas concentration could be observed from their graduated scale. For 40 years, all portable gas monitors have been 'direct-reading'. The International Safety Equipment Association (ISEA), founded in 1933, is a trade association that produces protective equipment, including DRPGMs. The ISEA advises checking the capability of these devices before use, with further testing when necessary. In 2008, NIOSH started a study in the direct reading instruments area with the foundation of the Direct Reading Exposure Assessment Methods (DREAM) initiative. The NIOSH Center for Direct Reading and Sensor Technologies (NCDRST), founded in May 2014, had the goal of harmonizing research and developing guidance on the use of 21st-century technologies in occupational safety and health.

The application of sampling sensors has progressed exponentially since remote wireless ones are largely used to monitor the environment, worksites, 'smart' buildings, and in agriculture and health. The increasing adoption of this kind of sensor is linked to their upgrade with wireless data transfer, using cell-phone or smartphone technology, and to the possible integration of data from space-dispersed sensors, to obtain clear exposure scenarios.[99] Nowadays, another relevant innovation is the availability of classic bench-top LC and GC system, coupled with the respective detector, as portable instruments,[100–103] bringing 'on-field' specificity and sensitivity, linked with versatility, something unthinkable only a few years ago.[104]

7. Limit Values History

In 1849, Peter Koffer suggested an exposure standard for carbon monoxide of 50 ppm. In 1874, Army Surgeon F. de Chamount proposed 200 ppm above outdoor levels as internal air quality standard value for carbon dioxide. In 1883, one of the first Occupational Exposure Limits (OELs) was set for carbon monoxide, using the data from the study of M. Gruber at the Hygienic Institute in Munich. In 1886, K.B. Lehmann proposed OELs for some organic solvents and irritant vapour; in 1912, R. Kobert produced a list of acute exposure limits for 20 compounds in the 'Compendium of Practical Toxicology'.[105] In 1916, South Africa established a permissible exposure limit of 8.5 million particles per cubic foot (mppcf) of air for dust, containing 80–90 % of quartz. The US Bureau of Mines in 1917 proposed an OEL of 10 mppcf for quartz. In the 1920s, a list of OELs for 27 chemical compounds was published in the 'International Critical Tables for Numerical Data'. During the same period, the US Bureau of Mines set OELs for 33 compounds. In 1930, a list of workplace maximum allowable concentrations for 12 substances was produced by the USSR's Ministry of Labour produced. In the 1940s, the American Standards Association (ASA) and of some industrial hygienists, founder of the ACGIH in 1938, proposed a list of 'Maximum Allowable Concentrations' (MAC values). The Thresholds Committee of the ACGIH established the first table of 63 MAC values – that will later become the classic TLVs. In 1946, the subcommittee on TLVs set values for 131 gases, vapours, dust, fumes, and mists, and 13 mineral dust.[1] The term 'threshold limit values' was introduced by Henry Smyth 1956. Before then, the maximum allowable concentration (MAC) was utilized.[12] The MAC list was first presented for use in 1946. The early years of exposure assessment, namely the 1930s and early 1940s, were associated with unofficial guidelines, such as that developed in the Dreessen *et al.*,[106] investigations for asbestos (1938). This study resulted in a guideline of five million particles per cubic foot of air based on what is now termed 'rough' or even flawed epidemiology. To understand the approach to the sampling of those years, very helpful is the 1936 edition of Industrial Dust by Drinker and Hatch, where the measure of millions of particles per cubic foot of air was proposed. The time-weighted-average exposure approach is attributed to Bloomfield (1933).[107] It can be concluded that, during this period, the goal of air sampling was to collect a series of short-term samples to characterize the variations in individual employee exposures. Understanding exposure variations were of engineering control significance since there were few guidelines for airborne agents and those that did exist were not considered firm numbers. The person assessing dust concentration during the 1930s and early 1940s were interested in controlling the sources of emission; the airborne contaminant concentration determined in the exposure assessment was key to that control. In 1945, ACGIH, by Warren Cook, proposed 132 TLV.[108] As late as 1958, in the standard reference *Industrial Hygiene and Toxicology*, edited by F.A. Patty, it was indicated that after establishing the location where additional control is necessary, the investigator should then devise the proper control method. The Walsh-Healey Public Contracts Act of 1956 established the threshold limit values as federal standards for contractors doing business in excess of $10,000 each year with the US government. In 1989, the Occupational Safety and Health Administration (OSHA) recommended that workplace air concentrations for 376 substances must be held below new permissible exposure limits; 350 of these limits derived from the 1987 table of 'Threshold Limit Values' by ACGIH.[109] To date, ACGIH has proposed the TLVs for over 600 chemical substances and physical agents, as well as over 30 Biological Exposure Indices for selected chemicals. These values are reviewed and updated annually by a committee of health professionals and many authorities have referred to them when establishing occupational exposure limits in their jurisdictions.

8. Ensure Data Quality and Validity: Laboratory Information Management Systems (LIMS)

Since its inception, the Laboratory Information Management Systems (LIMS) has been related to the IH industry to help guarantee data quality, validity, and ease of access in an IH laboratory setting.[110] A LIMS has become a must for laboratories in the environmental industry, due to the call for better data administration and set up to work with the most current instrumentation found in environmental laboratories. As instrumentation has developed, the quantity of data collected and needed to be accurately processed and saved has grown exponentially. The management system development started as an in-house program, then evolved to customized solutions, followed by the open-source system.

An example of an interesting LIMS development was Bika (Cape Town, South Africa).[83] The Bika Open Source LIMS program begun in 2001 as a prototype in the Western Cape wine industry. Due to the cost of pre-internet systems, in that period there was a need for economical, easy to use data management and instrument integration system. The number of web clients was increasing, but few laboratory data management systems were specifically web-based, often only web-enabled systems and there was no application of open source LIMS to chemistry. Bika 1 was created in 2004 in the modern web application server and CMS framework Zope and Plone, and it was released to the public in 2005. Since then, the system has seen constant growth thank utmost releases Inkosi 'Chief' LIMS 2 and Gaob 'King' LIMS 3, including microbiology, environmental management, IH and inter-laboratory proficiency testing. Bika LIMS 4 advanced into Senaite LIMS 1, a version characterized by enhanced performance and software optimization. Nowadays, Bika/Senaite LIMS is one of the most popular accessible open-source LIMS, helped to maintain the professional standards with low costs by users, developers and sponsors. Since 1994, Accelerated Technology Laboratories Inc. created the first commercially available Windows-based LIMS, powered by database engines like Oracle and Microsoft SQL Server. Always in 1994, Blaze Systems Corporation (Newark, DE, USA) purchased the Encompass LIMS business from Enviromatix and released its first version of Blaze LIMS in 1996. Other historical LIMS are Prolab.Q (Open.Co, San Pietro in Cariano, Italy) opened in 2001, and BTLIMS (BTLIMS Inc) started in 2002.

9. Industrial Hygiene Proficiency Analytical Testing Programs

To obtain accurate exposure data, the sampling and analytical methods used to characterize the work environment must yield reproducible results regardless of which laboratory performs the analysis. Proficiency testing aims to afford objective evidence to interested parties that a laboratory can produce data that are both accurate and repeatable for the activities recorded as its scope of accreditation. Through favourable proficiency testing data, a laboratory's competence can be confirmed. The Proficiency Analytical Testing (PAT) program was begun by NIOSH in 1972 with government laboratories only.[19] They were joined by commercial laboratories seeking American Industrial Hygiene Association (AIHA, Virginia, USA) accreditation in 1979. The AIHA program[111–113] proposes the Industrial Hygiene Proficiency Analytical Testing (IHPAT) for metals, silica, asbestos, organic solvents, formaldehyde, thermal desorption tubes, and diffusive samplers. Other proficiency tests organized by different bodies exist in the field of occupational health, particularly in the UK there is the Health and Safety Laboratories, in France the Institut National de Recherche et Sécurité and in Germany the Berufsgenossenshaftliches Institut für Arbeitsschutz.[114–116] ALASCA, which is the French acronym for Ability of Laboratories to Analyze Airborne Chemical Products, is a proficiency test that has been developed for four metal elements, which are cadmium, chromium, nickel and lead, and for three anions, which are fluoride, chloride and nitrate.[117] IHPAT Program, developed in the USA, has been modified and introduced in the Republic of Korea as the QC program since 1987. From 2000 onwards, studies have been continuously conducted investigating the legal and institutional administration and technologies for the technical application of the QC program by the Occupational Safety and Health Research Institute (OSHRI).[118] Other research groups created frameworks by carrying out interlaboratory exercises.

10. Conclusion

The air sampling and analysis for IH nowadays has developed into a fine science, with automated sampling and instantaneous analysis using all kind of sophisticated sensors. The strategies and devices for occupational chemical airborne contaminants presented here were entirely associated with their historical perspective, to highlight the constant evolution that has always characterized them. Moreover, nowadays commercially available means have been presented to offer the state of the art of air sampling in IH and to provide help choosing those who approach this theme. We have observed that a great effort is going into the development of reliable sampling/sample-preparation procedures, characterized by the simplicity of both the operations and the devices involved in the process. All sampling tools have seen an incredible evolution, particularly dust-sampling techniques have progressed from those distant days, out of necessity, with new particle size analyzer able to determine particle distributions at the press of a button, and sensitive analytical instruments analysing particles in trace amounts. The methods applied to monitor environmental xenobiotics pollution should allow not only direct monitoring of the fate and concentration of chemicals but also enable assessment of their effects and evaluation of the potential chemical hazard for humans.

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