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Cancer prevention in the workplace:

Precise measurement of VOCs

Butadiene, ethylene oxide and acrylonitrile – so-called volatile organic compounds (VOCs) – are important components in the manufacturing of plastics and intermediate products in the chemical industry. All three materials are carcinogens, however they can't be substituted in the production process. In this type of work, which must be regularly performed in polluted environments – like maintenance services for flanges and pipes or tank cleaning – strict exposure limits must be in place. Compliance with these limits is enabled by effective monitoring with specific measurement strategies and measurement devices.

Important raw chemicals in plastics production

Butadiene, ethylene oxide and acrylonitrile are actively produced as raw chemicals in the industry and are stored in tanks until further processing. Because of high vapour pressures, they occur in gaseous form. During transport around the plant facility, **leakages** may occur at transfer points and through valves. As a result, the hazardous substances can also be present in the air in open areas. Occasionally, the **tanks** or containers carrying these substances must also be cleaned and maintained. In every case, before maintenance work and inspections take place in such environments, clearance measurements must be taken – and employees must then be monitored as they carry out their work.

An exceptional challenge: the technical feasibility

Because of the carcinogenic properties of these materials, the **occupational exposure limits** and compliance with these limits come into particular focus. Most **measurement technologies** do not have the technical capability to observe and monitor these values precisely and continuously. At times in which employee protection becomes of more and more importance worldwide, the chemical industry is faced with an exceptional challenge: what can be done to protect employees from the hazards that come with their daily work tasks – and how do we implement this protection in an ideally cost-effective way?

Selected national occupational exposure limits

Country	Hazardous substance/Reference parameter		
	1,3-Butadiene	Ethylene oxide	Acrylonitrile
Australia	10 ppm (TWA)	1 ppm (TWA)	2 ppm (TWA)
Denmark	10 ppm (TWA)		2 ppm (TWA)
Germany (level of acceptance)	0.2 ppm	0.1 ppm	0.12 ppm
Germany (level of tolerance)	2 ppm	1 ppm	1.2 ppm
South Korea	2 ppm (TWA)	2 ppm	2 ppm
USA (OSHA)	1 ppm (TWA)	1 ppm	2 ppm
UK	10 ppm (TWA)	5 ppm (TWA)	2 ppm (TWA)

Sources: Dräger VOICE®[1], Gestis/IFA[2], TWA: Time-weighted average/8-hour shift

Imperative: Clearance measurements of confined spaces and immediate environment

Before work begins, particularly in the case of tank cleaning, clearance measurements are essential. These are the basis for a decision on whether and, when applicable, which protective equipment should be used when entering the contaminated areas. Due to being closed-in and having restricted ventilation, confined spaces such as tanks always contain potential Ex, Tox and Ox hazards. In the case of the carcinogenic substances butadiene, ethylene oxide and acrylonitrile, it's necessary to protect workers from acute toxic effects as well as to prevent chronic long-term health effects.

Only through clearance measurements can we be sure that local occupational exposure limits for butadiene, ethylene oxide and acrylonitrile are adhered to and that employees are protected from life-endangering concentrations of these substances. Otherwise, further measures such as airing out tanks until they have reached an acceptable minimum-concentration or the use of suitable protective gear is necessary. This applies to employees working inside as well as for anyone working in the immediate surroundings of the job site. Occupational exposure limits, in particular for carcinogenic substances, are continuously being tightened in many industrial nations – so it follows that the requirements for measurement strategies and methods are also increasing.

The optimal measurement strategies for clearance measurements in the workplace

For the detection of individual **volatile organic compounds** (VOCs) like butadiene, ethylene oxide and acrylonitrile, it is useful to initially carry out a pre-test on the sum of all VOCs. While acrylonitrile and ethylene oxide can be measured with an electrochemical OV or OV-A sensor, the use of a **PID sensor** (photoionisation detector) is advisable for 1.3-butadiene because it registers concentrations as low as 0.05 ppm. The choice of sensors should also always take desired or undesired cross-sensitivities towards other occurring substances into account.

Because these sensors only measure the present concentration of all volatile organic compounds in their sum, another differentiated analysis is needed. Only in this way is it possible to evaluate the potential risks of each individual hazardous substance present. If the sum-measurement reading of the PID or OV sensor is too high, subsequent selective measurements are needed to make it clear exactly which carcinogenic substance accounts for the highest proportion of the overall concentration.

Selective measurement strategies for the specific assessment of a situation

For selective measurement, short-term gas-detector tubes which can measure very low concentrations are suitable for specific hazardous substances – such as the Dräger-Tubes® Acrylnitril 0,5/a, Ethylenoxid 1/a or for 1.3-butadiene, the Dräger-Tube Chloropren 5/a.

The advantage of short-term tube devices is that they are less expensive to purchase. Due to the pump strokes and reaction times, however, the measurement process can take a few minutes. Alternatively, for an exact analysis, a probe collector can be sent to a laboratory. This is still a common methodology because the analytical accuracy positively contributes to overall safety. However, in many cases, the time and cost requirements of this method, especially when several measurements are needed, are factors that can negatively affect process efficiency.

In the case of 1.3 butadiene, it's possible to substitute the measurement by the use of a PID-sensor with a combined gas chromatograph. This combination device combines pre-tests with selective tests, therefore simplifying and shortening measurement processes. Two measuring modes, one **broadband measurement** in scan mode and one selective measurement in analysis mode, eliminates the need to carry out manual tube tests and increases safety through **laboratory-quality** measurement results. It incurs higher procurement costs – but at a higher frequency of use, when broken down per measurement, this could be worth it.

In large companies that require a lot of measurements, documentation obligations mean that a large amount of data can create high administrative expenses. Modern digital data-transfer methods reduce the potential for error during documentation and save time thanks to less need for manual steps.

Monitoring of work in risk areas

After the successful clearance measurement of an area and resulting work permission, work can begin. Work areas are classified as hazardous based on the risk assessment of each area.

Continuous personal **monitoring** can be achieved through use of gas detection devices carried on the body of each worker (personal area monitoring = PAM). The continuous monitoring of a work area normally takes place with an inexpensive but less sensitive OV sensor. The alarm threshold is adjusted depending on the risk. When an alarm is activated, work must stop immediately. Because of the low sensitivity of OV sensors, regular selective control measurements should also be carried out. Their frequency depends on precise risks in accordance with risk evaluations, which also determines the preferred measurement methods. In principle, these repeated measurements correspond to the clearance measurement method.

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The measurement strategy chosen by a facility safety officer depends on three key factors:

- The measurement quality, which is oriented to the level of safety desired based on the risk assessment. The way the results are displayed, the accuracy of the indicator and the required selectivity determine the quality.
- The measurement convenience when carrying out measurements. This includes the number of steps, how fast data is available onsite and whether operation is fail-safe.
- The use-frequency of the devices, which determines the cost per measurement. Higher procurement costs can pay off fast when they are calculated against cost per ongoing use.

Decision support: Which measurement strategy is suitable for which purpose?

Method	Laboratory	Gas detection tubes with pump	Measurement devices for sum measurements and selective measurements of VOCs	PID with gas chromatograph
Example device		Dräger-Tubes® with Dräger accuro	Dräger X-am® 8000	Dräger X-pid® 9000/9500
Procurement costs[3]	*None* (if used as external service)	*Low* Pump: Dräger accu-ro-Set: approx. 300 €	*Average* Dräger X-am® 8000 with Ex-, O_2-, CO-, H_2S- and PID sensors: approx. 3,000 €[4], incl. charging device	*High* Dräger X-pid® 9000/9500: approx. 18,000 €[4]
Costs per measurement[3]	*Very high,* approx. 70 €	*Average –* depending on use Cost per tube: 5–10 € Time needed: 4–8 minutes → 4 € Assumption: 10.50 € per measurement on average	*Low* Assumption: 6.58 € per measurement on average[7]	*Very low* Assumption: 0.66 € (only labour costs)
Specifics	Very precise substance-specific measurement, long waiting times due to transport routes	Good measurement quality, selective measurement, no maintenance or lead time	Fast as pre-test Use is supported by a digital assistant.	Accurate readings in low range, selective, immediately available onsite, easy to use. No disposable items necessary. Compensates for external influences (temperature and humidity)

Further aspects	Error potential while sampling, training required, thus higher costs for service providers	Requires practice, several minutes needed per measurement, disposable items required. Outside influences, such as temperature and humidity, affect measurement results.	Only pre-test option, no selectivity, occasional combination with selected pre-tubes. Training needed. Maintenance and preparation steps necessary. Digital data transfer possible	Digital data transfer possible Maintenance and preparation steps necessary
Evaluation of measurement quality in total[8]	10	5	6	9
Evaluation of measurement convenience in total[8]	1	5	7	10

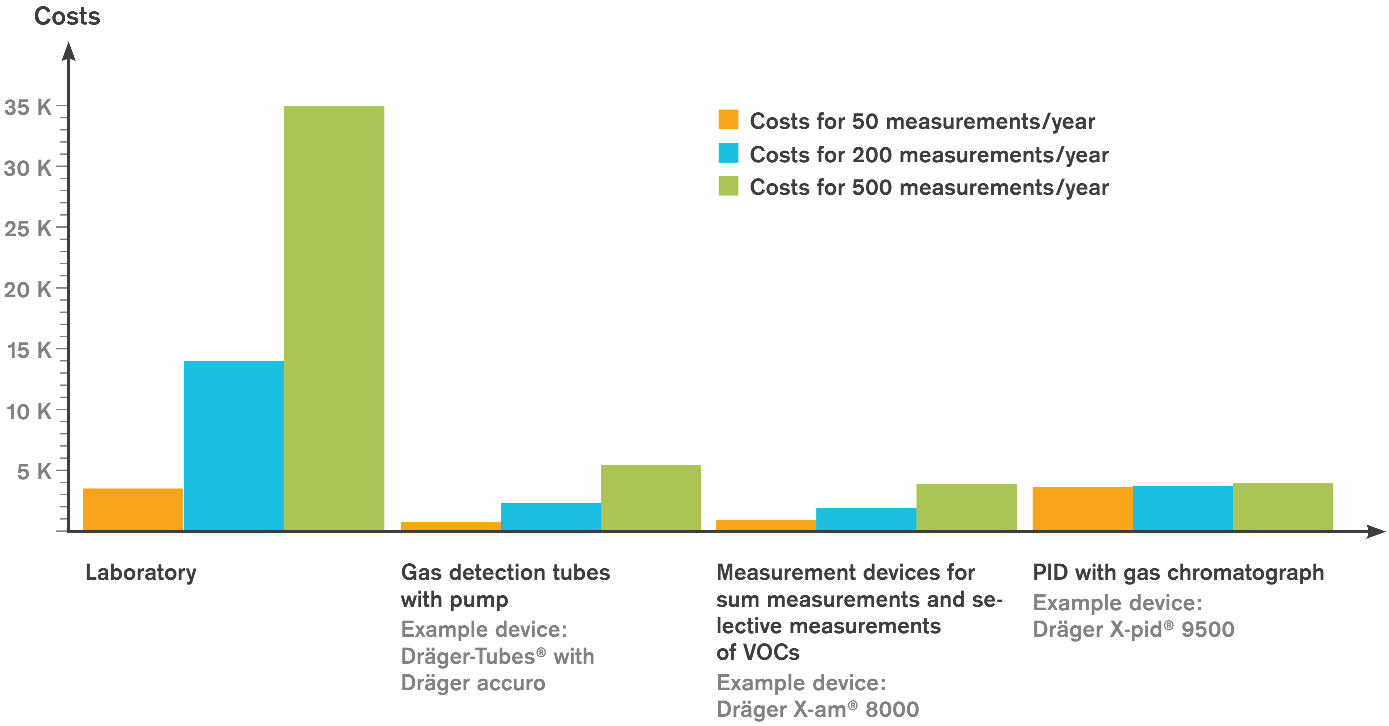
Decision support: Use frequency as benchmark

For companies with high measurement needs (upwards of ca. 500 measurements/year) and facilities with high toxic risk from carcinogenic substances like butadiene, ethylene oxide and acrylonitrile, the use of an electronic PID or OV sensor is suitable for a pre-test, with the implementation of selective re-measurements on a case-by-case basis. In our example, every second measurement was selectively verified. The use of a combination PID-measurement device with a gas chromatograph is particularly efficient in such a case, because no additional costs are accrued with each further measurement. At the same time, safety levels are improved because each selective measurement can be carried out easily, quickly and safely.

With average use frequency (ca. 200 measurements/year) a measurement device with a PID sensor is also appropriate. Pre-tests and selective tests are rolled into one work step. With relatively frequent readings, this can bring about potential savings when compared to exclusive selective measurements.

With low use frequency (around 50 measurements/year), selective tests with detection tubes, as well as occasional complementary laboratory tests to ensure measurement accuracy, are an appropriate measurement method. Supplemental non-selective pre-test devices with high ease-of-use are a viable alternative.

Choice of measurement devices in relation to use frequency



LEGEND:

a) Cost for 50, 200 and 500 measurements result from purchasing costs/year + number of measurements x costs per measurements

b) Example for laboratory costs by external service cExample: Selective measurement, as necessary for 50% of the use cases

[1]https://www.draeger.com/de_de/Alcohol-and-Drug-Detection/Online-Service/VOICE-Gefahrstoffdatenbank; accessed: 07/08/2018

[2]https://www.dguv.de/ifa/gestis/gestis-stoffdatenbank/index.jsp; accessed: 07/08/2018

[3]Pure purchasing costs of device as global benchmark, split on expected 5-year device lifespan; maintenance costs and costs for replacement parts are not included for transparency purposes.

[4]Estimated average market price. Product not yet available in market. Status as of 2018.

[5]Estimated average costs per measurement; incl. Disposables and labour time. Labour time = duration of measurement x average labour wage (assumption: 40 €/h). A tube measurement takes an average of 6 minutes which equals 4 € labour costs.

[6]A tube measurement takes in average 6 minutes => 4 € labour costs

[7]Assumption in the calculation example: Every second sum measurement is validated by a selective tube measurement. Average costs: 1. Sum measurement (2 min.)= 1.33 €, 2. Tube measurement 6.50 € + 4 € / 2 (as necessary for 50% of the use cases)

[8]On a scale from 1-10. 10 = very high; 1 = very low

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