Benzene measurement strategy

In the petrochemical industry, benzene vapors can hardly be avoided. Work-related cancer, on the other hand, can be. But it requires precise monitoring of exposure to benzene using the right measurement strategy.

Precisely identifying benzene in even low concentrations

Knowledge of the carcinogenic effect of benzene on the human body has grown in recent years. Public awareness of the topic has also grown – as have regulatory requirements for companies to protect employees against inhaling benzene vapors.

In the 1980s, threshold values of up to 50 ppm were permissible. Today, OSHA defines a permissible exposure limit (PEL) of 1 ppm (measured as a time weighted average – TWA). The limit recommended by NIOSH (Recommended Exposure Limit – REL) is clearly below that at 0.1 ppm (TWA). And in some countries, permissible levels are even lower. In Germany, for example, the so-called "risk acceptance concept" of TRGS 910 defines tolerable exposure at 0.6 ppm. In addition, the accepted exposure level is currently 0.06 ppm, but will be reduced to 0.006 ppm in 2018.

These strict guidelines pose a challenge for Health, Safety + Environment officers (HSE), since very few technologies are capable of reliably indicating these extremely low values. Ideally, HSE officers are already taking steps to avoid exposing their employees to carcinogenic materials where possible.

FACTS & FIGURES

Benzene

Formula: C_6H_6
Identifiers: CAS 71-43-2,
Label required: Flammable liquid
Explosion limits, % by volume: LEL: 1.2; UEL: 8.6
Health rating (NFPA): 3 (dangerous)
Odor threshold: 0.78 ppm
Health effects: Eye, nose and respiratory tract irritation leading to headache, dizziness, convulsion and coma.
Chronic: Cancer (leukemia)

LIMIT VALUES FOR BENZENE

EU	D		USA	
European Directive 2004/37/EG	German occupational health and safety limit (AGW)		OSHA (PEL)[1]	**NIOSH (REL)[1]**
1 ppm / 1 ml/m³	0.06 ml/m³ acceptance concentration	**TWA**	1 ppm	**0.1 ppm**
	0.6 ml/m³ tolerance concentration	**STEL/CEIL-C(15-min.)**	5 ppm	**1 ppm**

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Different measurement tasks

Measuring benzene in the workplace can involve very diverse tasks, such as clearing a tank for maintenance work, measuring the average contamination of a work area, or checking the level of temporary peak exposure values. Furthermore, different companies implement regulations very differently. While some companies clear all work areas once a year, others examine individual work steps and attempt to precisely locate peak exposure sites. The goal is to make these critical work steps safer through the use of technical and organizational methods – and even additional breathing protection.

[1] *http://www.acgih.org/forms/store/ProductFormPublic/2016-guide-to-occupational-exposure-values*

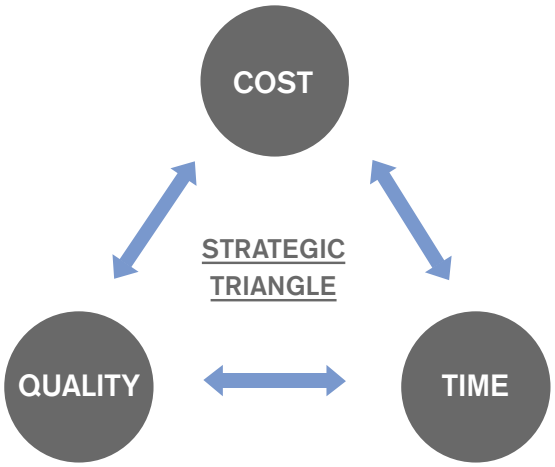
Balancing quality, time, and cost

Three criteria determine the selection of measurement methods: quality, time, and cost.

Quality pertains to the precision of the measurement results. Does the benzene concentration need to be measured selectively or is it sufficient to determine the sum value of all hydrocarbons in the air?

The factor of **time** is becoming increasingly important due to the pressure to increase efficiency. The faster a method delivers reliable results, the sooner work may continue after clearance. An important advantage of on-site measurements versus laboratory evaluation is the time that is saved – since evaluation is possible directly at the task location, where further measures may be decided upon.

In terms of **cost,** the number and frequency of measurements that need to be completed play a central role. Detector tubes, for example, offer an economical solution. The purchasing costs are low, and there are nearly no maintenance costs. However, if a company performs many measurements at a continuous rate, reusable solutions are more affordable.



Solution: Combining different methods intelligently

With benzene measurement, there is a difference between selective and non-selective methods. Isolated evidence can be gained from detector tubes, chips and diffusion collectors, as well as from laboratory results. Photo-ionization detectors (PID), on the other hand, only measure the sum of all volatile hydrocarbons in the air. Therefore, PIDs need to be combined with selective methods.

ALARMING RESULTS

In 2014, NIOSH conducted a field study[2] in the fracking industry to examine the level of exposure of employees to benzene gases in the atmosphere.

The results were as follows:

- 15 of the 17 samples exceeded a value of 0.1 ppm
- Two samples reached more than 0.5 ppm
- During certain work, the 15-minute median values of 1 ppm were regularly exceeded
- At open hatches, peak concentrations of up to 200 ppm were measured
- An Ex measurement device showed up to 40% of the lower explosion limit of a hydrocarbon gas concentration

[2] *Esswein, E., Snawder, J. King, B. et al. Preliminary Field Studies on Worker Exposures to Volatile Chemicals during Oil and Gas Extraction Flowback and Production Testing Operations. Niosh Science Blog. https://blogs.cdc.gov/niosh-science-blog/2014/08/21/flowback-2/ (assessed: 2016/10/17)*

OVERVIEW OF ADVANTAGES AND LIMITATIONS OF VARIOUS TECHNOLOGIES

Laboratory measurement

Suitable for clearance, workplace monitoring, spot measurement

In spite of a relatively high time and cost investment, laboratory measurement is widely popular, since most field measurement methods are limited in terms of selectiveness and precision (see overview). In the laboratory, on the other hand, extremely low or high concentrations can be determined reliably.

This requires on-site sampling, which normally involves a pump and a suitable collection medium. The waiting time for results depends on how well the transfer of the sample to the laboratory is organized. The evaluation itself can usually be completed quickly.

Passive collectors

Suitable for workplace monitoring

Passive or diffusion collectors (so-called "badges") consist of a collection medium, such as active charcoal, and a strip positioned before it that is in contact with the surrounding air. If the exposure of a person needs to be monitored, then a passive collector is fastened to the clothing at the inhalation area. Due to the relatively low concentrations of substances in the air of interior rooms, sampling times from one day to several weeks may be required to identify substances in the relevant concentration range. The badge is evaluated in the laboratory, while the collected substances are evaluated selectively. In any case, only average values may be recorded and exposure peaks are included in the average value.

HISTORICAL MILESTONES: FIRST BENZENE MEASUREMENT IN THE FIELD

It was quite cumbersome and not very fast with 40 double strokes, but for the gas measurement technology of the time, it was a small revolution. In 1939, the Dräger-Schröter hand pump enabled benzene measurement in the field for the first time. Its functional principle was that drawn-in air was collected with active charcoal and extracted through alcohol with the help of the pump.

The alcohol solution was left in a test tube that contained substrata of formalin sulfuric acid. The benzene concentration could be read from the reaction.

Detector tubes

Suitable for clearance, spot measurement, leak searches

Detector tubes can be used to detect benzene precisely, quickly, and economically. The new 0.25/a Dräger-Tube® measures to the lowest concentrations above 0.25 ppm. Measuring benzene using detector tubes is fast and simple. The tubes can easily be operated by non-experts using a hand pump – even in Ex areas. That's why detector tubes are suitable for air analysis in tanks and containers and for detecting leaks. It is also possible to use them for measuring contaminations in certain work areas and detecting peak concentrations.

Chip measurement system

Suitable for clearance, workplace monitoring, spot measurement

With the Dräger chip measurement system (CMS), benzene-specific measurements can be conducted on-site. CMS combines the advantages of Dräger-Tubes with those of an optoelectronic evaluation system. The measurement is taken using a substance-specific chip, which is inserted into the analyzer. After one to ten minutes, the analyzer provides the result – the lower the concentration, the longer the measurement will take. Two ranges may be measured: 0.05 to 2.5 ppm or 0.2 to 10 ppm.

Photo-ionization detection

Suitable for clearance, workplace monitoring, spot measurement

Photo-ionization detectors are ideal for locating hydrocarbons – especially if they are present in very low concentrations. However, they cannot measure benzene selectively. Therefore, if a critical hydrocarbon level is detected after a PID measurement, then a follow-up measurement is carried out using detection tubes. Alternatively, a so-called selection tube may be installed beforehand for benzene detection, which filters other hydrocarbons out of the air and only permits benzene into the PID sensor. With this method, the result is available after a few minutes. Selective measurement with tubes or pre-installed tubes may be omitted if the overall contamination by hydrocarbons is sufficiently low.

One advantage of PID devices is their ability to measure continuously and produce a "concentration profile" using the results of a workplace across an entire shift. This makes it easy to detect peak exposures that occur during certain work steps. The disadvantage compared with other benzene measurement methods is the high cost of the devices.

FEATURES OF DIFFERENT MEASUREMENT TECHNOLOGIES

Method	Is selective measurement possible?	Measurement range	On-site application?	Time factor	Costs
Laboratory	Yes	**Practically unlimited**	No	**Several hours**	High
PID (e.g. Dräger X-am® 8000)	In combination with benzene selective tube	**From 0.05 ppm to 2,000 ppm (depending on sensor type), gas: isobutene**	Yes	**1 minute**	Medium
Detector tube Dräger-Tube®	Yes	**0.1 ppm or 1 to 2,000 ppm**	Yes	**5 minutes**	Low
Chip measurement system	Yes	**From 0.05 ppm to 2,500 ppm (depending on the chip)**	Yes	**1 to 10 minutes**	Medium

Tested application for efficient clearance

PIDs with pre-installed tubes, detector tubes, chip measurement systems, and selective evaluation of benzene in measurement laboratories are all suitable for clearance in areas such as tanks and other confined containers or rooms.

The combination of a PID and detector tube is a cost-effective method. During a pre-test, the PID measures the sum of all occurring hydrocarbons. From this it is possible to calculate the expected benzene concentration. This knowledge provides the basis for deciding if further ventilation is required.

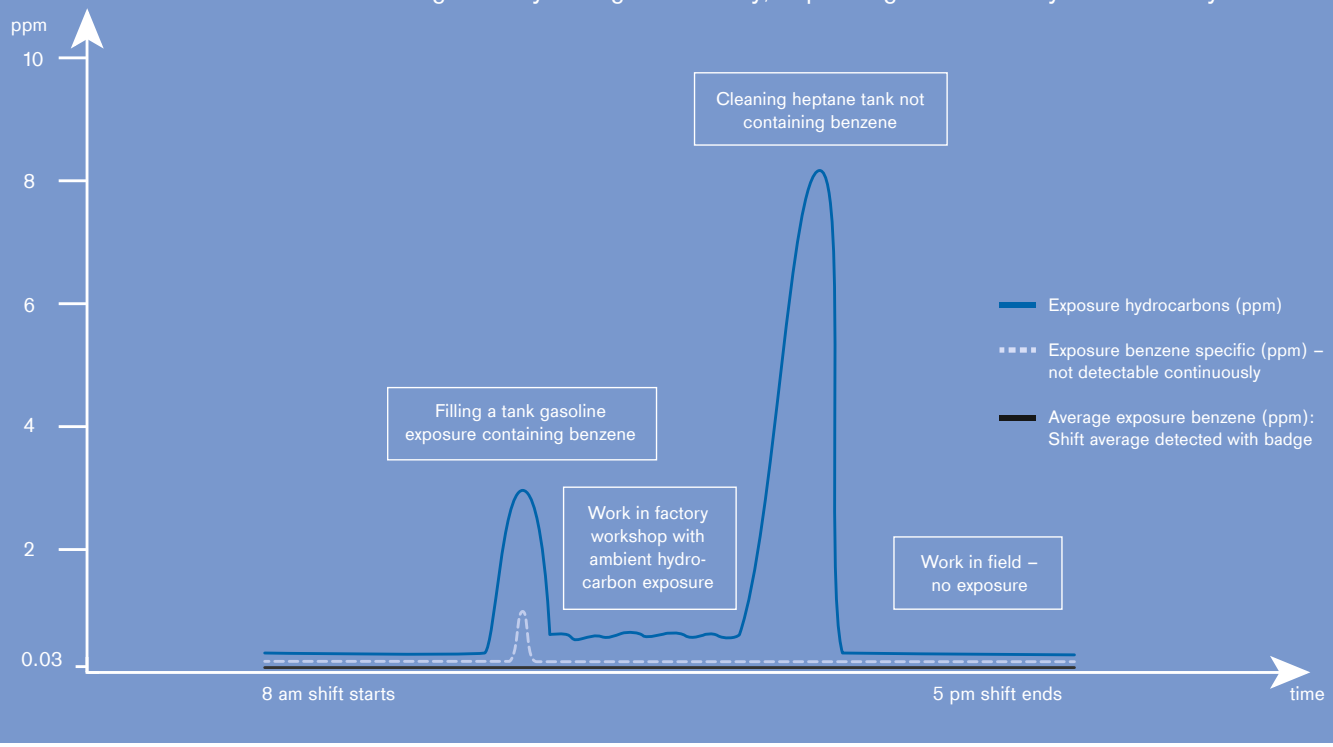
For example, if the sum of hydrocarbons in a benzene tank is below the defined maximum value of 10 ppm during the pre-test, then selective measurement in a second step measures the benzene value using a pre-tube for the PID, detector tubes or a chip measurement system. The advantage of this process is fast results, which enable safe decisions and improve cost-effectiveness through the use of specific tubes.

Reliable workplace monitoring

The amount of benzene to which employees are exposed during a shift depends on their activities and the resulting concentrations involved. In the petrochemical industry, contamination levels often show significant fluctuation. While exposure can briefly be very high during refilling, sampling, and other work at open hatches, it is practically zero in office areas and outside.

CHANGING CONTAMINATION

The benzene concentration to which an employee is exposed to may fluctuate significantly throughout the day, depending on the activity. A case study.



Diffusion collectors, such as ORSA badges, are suitable for continuous monitoring. PID devices may be used, because they quickly react to changes in concentration and immediately indicate if limits are exceeded. Another advantage of PID devices is data recording: All measurement values are stored for later analysis.

To calculate the average benzene concentration in the workplace, a sample should be taken across the entire work period (normally an 8-hour shift), or a series of sequential samples of 30 minutes each should be measured.

In order to determine exposure peaks in the context of NIOSH-REL, samples are taken at the corresponding task location – using detector tubes or other suitable collection medium for laboratory analysis later.

Ideally, the sample should be taken from a location where the composition of the atmosphere represents as accurately as possible the air that the employee will be inhaling. The US Department of Health and Human Services recommends that at least three samples of 15 minutes duration each should be taken.[3] The sample with the highest value is given as the maximum concentration.

Combination measurement methods offer cost savings

In practice, companies usually require different measurement tasks. For example, further observation is often required after clearance. Each benzene measurement method usually has a specific focus. In other words, it is ideally suited to clearance or monitoring tasks, but not equally for both. For this reason, it makes sense to combine methods – especially if benzene needs to be detected in very low concentrations, such as at the NIOSH-REL level. With an intelligent strategy, the cost of measuring benzene concentrations may be reduced noticeably.

DRÄGER SOLUTIONS FOR THE COMBINATION STRATEGY

Clearance

The pre-test is completed with the Dräger X-am® 8000/PID: Alarm thresholds are set according to the hydrocarbon qualification, e.g., 10 ppm for a petroleum tank

Selective measurement

If the total sum of volatile hydrocarbons is < 10 ppm, then another selective measurement for benzene is taken with tubes, CMS, or PID with a pre-installed tube

Monitoring

Monitoring work with the Dräger X-am® 8000/PID

Random samples

Regular laboratory analysis of random samples for qualification of hydrocarbons (sum of VOC to benzene)

[3] *Occupational Safety and Health Guideline for Benzene. https://www.cdc.gov/niosh/docs/81-123/pdfs/0049.pdf (2016/10/17)*

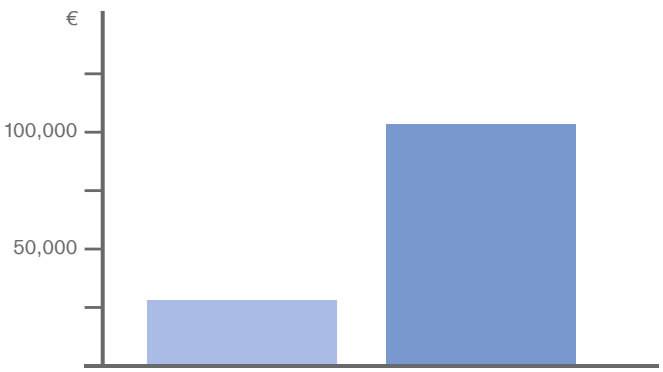
Combination strategy saves up to 75% over laboratory measurement

What is the relative cost between tubes and laboratory clearance methods?

Here is a sample calculation from a petrochemical plant in Germany:

- Assumption: Plant with 15 measurements per day at OSHA-PEL (1 ppm) calculated on 230 workdays per year
- Measurement strategy for clearance in EU and ROW: Pre-test with Dräger X-am® 8000 (PID) at a rate of 0.46 € per test, whereby approximately 20% of the measurements were followed by a selective measurement of benzene at a rate of 6.26 € per tube measurement (This can be Dräger-Tube® for benzene or a pre-tube for the X-am® 8000 for selective measurement)
- Only 20% of all clearances are checked with random samples in the laboratory (at a rate of 30 € per test)

Precise and cost efficient



Pre-test measurement strategy with PID, selective with tubes + CMS; laboratory testing. Total amount consists of 15 PID tests for 0.46 €, 4 tests with tubes for 6.25 €, 3 lab tests for 30 € on 230 days.

All clearance measurements for benzene in the laboratory. Total amount: 15 laboratory test at a rate of 30 € on 230 days.

ON-SITE MEASUREMENT IN FIVE MINUTES

It's fast, easy and economical. The new Dräger-Tube® for benzene enables selective measurements to be taken directly on-site. In the range of 3 to 10 ppm, one stroke is enough, and for values between 0.25 and 2 ppm, five strokes deliver precise results in just five minutes.

SPECIALIST FOR HIGH AND LOW HYDROCARBON CONCENTRATIONS INCLUDING BENZENE

To measure hard-to-detect hydrocarbons, you can fit the Dräger X-am 8000® with one of two high-performance PID sensors. The PID HC covers a measurement range of 0 to 2,000 ppm (isobutene). The PID LC ppb is particularly suited for a measurement range of 0 to 10 ppm (isobutene) with a low resolution in the range below 1 ppm.

For benzene-specific measurements, the X-am 8000® can be used with a pre-tube. The advantage: you only need one measuring device for this application, which significantly reduces the costs of purchasing, maintaining and transporting devices in use. The use of the pre-tubes is supported by a built-in assistant.

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