Guidance document : Implementation of a benzene OEL of 0.2 ppm in refineries and chemical plants producing or handling benzene

January 2021

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Disclaimer

This document is intended for information only and sets out guidelines for implementing an occupational exposure limit (OEL) of 0.2 ppm in refineries and chemical plants producing or handling benzene including storage and handling of benzene containing streams.
This information is provided in good faith and, while it is accurate as far as the authors are aware, no representations or warranties are made with regards to its completeness. Each company, based on their individual decision-making process, may apply these guidelines, in full or partly or apply any other adapted measures.

It is intended that this document is a living document and to update it based on feedback and additional input received from Petrochemicals Europe and Concawe members.

No responsibility will be assumed by the authors in relation to the information contained in this guidance document.
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EXECUTIVE SUMMARY

The current binding OEL in Europe for benzene is 1 ppm, although some countries, such as the Netherlands and Germany, have implemented in their national legislation a lower OEL. In 2017, EU commission started work on a review of the existing OEL for benzene. Final retained OEL values for these components will be part of the 4th Amendment of the CMD (Carcinogenic Mutagenic Directive) that is planned to be published in the official EU Journal in H1 2021. The commission proposal that has been submitted to the EU parliament and the EU council proposes an OEL for benzene of 0.2 ppm, 4 years after publication in the official EU journal, with an interim value of 0.5 ppm after 2 years.

The objective of this document is to provide some guidance to refinery and petrochemical sites where benzene containing streams are being handled on how to develop an implementation plan to respect an OEL of 0.2 ppm.

First the legal implications of respecting a given OEL are clarified. Then the various steps to develop an implementation plan to respect the OEL are discussed.

Main steps in the process are.

- Identification of the various places in a refinery or petrochemical site where emissions of benzene occur that could result in an exposure of workers to above 0.2 ppm and identification of tasks where exposure of 0.2 ppm could occur.
- Develop an investment plan to reduce emissions of benzene at identified areas or tasks where exposure to benzene could be above the OEL value.
- Develop organizational measures that help to reduce exposure to benzene below the OEL during specific tasks.
- Implement an exposure monitoring plan to demonstrate compliance with the OEL.

This document is the result of input of a number of HSE experts working for Petrochemicals Europe and Concawe member companies. As indicated in the disclaimer, the document does not aim to be exhaustive nor complete. However, this document is a living document and will be updated depending on the feedback of refineries and petrochemical sites on the pertinence and usefulness of this document, as well as additional information made available.

Comments can be sent to Philip de Smedt, APA manager (pdsd@cefic.be), who will collect comments and update the document if sufficient new information is received

1. Introduction :

Benzene is a well understood human carcinogen. here is a vast literature on toxicity and carcinogenicity of this substance.
To protect workers in the workplace environment, the CMD (Carcinogenic Mutagenic Directive) 2004/34/EC sets a binding occupational exposure limit (OEL) of maximum 1 ppm for all EU, although members states can opt to set a lower OEL limit

In 2017 the Commission launched the process to revise the current EU-wide occupational exposure limit for benzene. The revised values will be part of the fourth amendment of the CMD.
First the Risk Assessment Committee (RAC) of ECHA was asked scientific opinion on new OEL value. In March 2018, RAC published their report and proposed a value of 0.05 ppm for benzene stating that there would no residual risk for cancer below 0.05 ppm.
Remark: Since the RAC opinion was published, a team of toxicologists and other health experts from the Lower Olefins and Aromatics REACH Consortium (LOA) has carried out more detailed work on this subject. The expert team has concluded that ECHA applied overly conservative safety factors in its assessment and that based on available scientific data, there is no residual cancer risk below 0.25 ppm.

Taking the RAC opinion, as well as a socio-economic impact assessment report by COWI into account, the Working Party Chemicals (WPC) and the Advisory Committee on Safety and Health at work (ACSH) recommended in 2019 to set the binding OEL for benzene at 0.2 ppm after four years of publication of the new binding OEL value in the official legislative journal of the EU, with a transition via 0.5 ppm after 2 years of publication. In September 2020, EU commission published its proposal for the legal text of the CMD 4th amendment, which essentially is in line with the WPC and ASCH opinion.
This proposal is, at the time of writing this document (January 2021), being discussed in EU parliament and EU council and is expected to be voted into law middle H1 2021.

The economic analysis that Triskelion[1] carried out at the request of Concawe and APA (a sector group of Cefic and Petrochemicals Europe) that, while in most refineries and petrochemicals plants handling benzene, exposure of workers is on average below 0.2 ppm, most plants/sites will still require significant investments to ensure that this exposure level is guaranteed at all locations in the plant and during all tasks being carried out with a potential for exposure to benzene The Triskelion report estimates these costs for EU refineries and petrochemical sites at around 1 billion EURO and operational costs at around 250 Million EURO/year. Some of the investments required may only be possible during turnarounds, therefore, to be compliant by implementation date of 2025, development of an investment plan needs to start now (i.e. the publication date of this document).

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[1] Socio-Economic Analysis of proposed Occupational Exposure Limit for Benzene. Triskelion. March 2019. The executive summary of this report can be downloaded from the APA website.
https://www.petrochemistry.eu/sector-group/aromatics/

An additional issue is how to verify compliance. To avoid continuous monitoring of all personnel in areas where there is a possibility of exposure to benzene, schemes such as EN689:2018+AC2019 can be used. However, such schemes request that during specific measuring campaigns all results are below 10 to 20 % of the OEL, or, using a statistical approach with more measurements, less than 5% of exposure with 70% of confidence, exceed the OEL. The monitoring methodology should be able to detect (limit of quantification LOQ) at least 1/10th of the OEL, i.e. 0,02 ppm.

This document tries to provide refinery and petrochemicals sites some guidance on how to develop this investment plan as well as organizational measures that may be required to achieve compliance with an OEL of 0.2 ppm.

2. Legal implication of a benzene OEL = 0.2 ppm

Occupational exposure limits (OELs) are airborne concentrations which indicate levels of exposure that protect health from effects of a chemical substance in the air of a workplace[2]. Such limits are set by regulatory authorities at European Union and national levels, taking into account available information and the most recent data on the hazards of a substance, particularly with respect to carcinogenicity, mutagenicity and toxicity to reproduction, and on the acute effects of exposure.
Occupational exposure limits are intended to be used as a tool to control exposure via inhalation for normal working conditions in workplaces.
The long-term (8-hour TWA) exposure limit is intended to control such effects by restricting the total intake by inhalation over one or more work shifts (usually a 8-hour work shift). Other effects may be seen after brief exposures. Short-term exposure limits (usually 15 minutes) may be applied to control these effects. For those substances for which no short-term limit is specified, it is recommended that a figure of three times the long-term limit be used as a guideline for controlling short-term peaks in exposure.

OELs for volatile substances, such as Benzene, are usually expressed both in parts per million by volume (ppm) and/or in milligrams per cubic meter (mg/m^3). The value in mg/m^3 for a given concentration in ppm depends on the temperature and pressure of the ambient air, which vary over time. Therefore, conversion calculations are based on a standard set of typical conditions. For benzene at 20°C and 101,3 Kpa, 1 ppm corresponds to 3,25 mg/m^3.

OELs set by European regulators have been subject to a tripartite consultation involving member states, the industry and trade unions.

[2] For non-threshold Carcinogens or Mutagens, there may be no safe value. In this case, OEL is a compromise value where health risk are non zero but considered acceptable, based on socio-economic analysis.
Remark : according to RAC and benzene experts from LOA, benzene is currently regarded as threshold chemical.

Note that member states can impose in their local regulations more constraining values than the binding European OEL (currently 1 ppm). This is already the case in some countries, such as Germany, the Netherlands, Denmark, Sweden, Poland, …

Compliance with an OEL demonstrates control of the exposure to Benzene for workers is achieved. One method to confirm that exposures do not exceed the OEL is to conduct occupational hygiene monitoring of workers using competent persons and validated sampling and analytical methods. In some member states, the application of the new EN689 standard that specifies a strategy to perform representative measurements is imposed or strongly advised or – like in France – the local regulation is inspired on it. As a practical consequence, measures have been taken to avoid exceeding 10%[3] of the OEL. For example, this can mean that before handover of equipment for maintenance or turnaround works, the equipment must be drained, purged and/or chemically cleaned until residual benzene vapors are less than 10% OEL. If this is not the case, further risk management measures including the use of specific RPE need to be applied.
Other means to demonstrate adequate control are professional judgement from experienced competent persons, biological monitoring of metabolites of benzene or urinary benzene and use of exposure models.

The proposed OEL of 0.2 ppm for benzene is an 8-hour average value. Industry must ensure that workers are not exposed to airborne concentrations of benzene averaged over 8 hours greater than 0.2ppm. Although there is no Short-term exposure limit (STEL) set at European level, it is recommended that exposure be less than 0.6 ppm averaged over 15 minutes. Those countries which already included STEL in their local regulations may be expected to set a new STEL when transposing the European OEL in their national regulation.

3. Develop your implementation plan

The following steps are recommended to set up your implementation plan

- Step 1: make an inventory off all streams and equipment which contain benzene and where they are located.
- Step 2: for those streams, make an inventory of your emissions points (including fugitive emissions) and tasks leading to exposure.
- Step 3: check exposure/emission data bases and identify relevant historical data on exposure and emissions.
- Step 4: perform additional monitoring where there is insufficient data available
- Step 5: evaluate potential projects and operational measures.
- Step 6: prioritize your implementation plan.

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[3] I tis also possible to allow put exceedance limit at 20 % but then more monitoring data are required.

These steps are developed in more detail below.

STEP 1: INVENTARISE THAT COULD LEAD TO BENZENE EXPOSURE

The first step is to identify all areas, equipment and streams in the site that contain benzene. We recommend that all streams or areas where benzene content is bigger than 0.1 % are taken into consideration.

STEP 2: INVENTARISE YOUR EMISSION POINTS AND TASKS LEADING TO EXPOSURE

Having identified the areas and streams in the site where benzene is present, you should next identify where and how emissions could occur.
Ideally, this should be done by a multidisciplinary team, where everyone puts in their expertise and experience, supported by any easily available data.

The following gives an initial and non-exhaustive overview of potential emission sources in a refinery and petrochemical plant handling benzene containing streams.

- Plant piping and equipment: any stream containing more than 0,1 %vol benzene should be seen as a potential source of fugitive emissions necessitating investment. Fugitive emission sources are; pumps seals, valves, flanges, ….
- Analyzer houses (vents)
- Wastewater treatment plants (especially the floatation and decantation units). Best Available Technology (BAT) is that these plants should be closed units, however many wastewater plants may still have open parts and in this case, these wastewater plants may sometimes be the area in the site with the highest benzene background levels. People working on such utility areas may underestimate the risk, because they are not familiarized to the risk of benzene exposure to the same extent as workers operating in benzene processing units.
- Tank farm: e.g. feedstock. Tank farms can represent an important part of the fugitive emissions of the plant. But from an occupational hygiene point of view, exceedance of limit values is rather rare in this area, unless very specific tasks are performed, such as sample taking (open sample points) or accessing tank roofs.

Exposure can also occur during execution of tasks such as.

- Maintenance of equipment during normal operation, if not properly emptied and cleaned before handover (e.g. pumps, valves, …).
- Sample taking - especially on streams with low benzene content, i.e. where no Dopak (or similar closed system) samplers are installed.
- Laboratory analysis
- Preparation of turnaround. Draining, opening of equipment,
- Equipment entry. If confined space procedures are well respected, this shouldn’t be the case. But in case the equipment couldn’t be properly emptied, cleaned,

ventilated, isolated before (e.g. due to dead ends, deposits, use of some solvents, etcetera), this may be the case.

- Industrial cleaning (high pressure and vacuum cleaning) of equipment. Special attention should be paid to activities with vacuum cleaning units not equipped with a scrubber on the exhaust.
- Accidental exposure in maintenance workshop (e.g. valve and pump shops) due to contamination and/or residual product in dead ends.
- Maintenance of equipment during turnaround.
- Calibration of instrumentation
- Loading/unloading operations, especially during connecting/disconnecting of loading arms and flexibles (less during loading/unloading itself, if a vapor recovery unit is available).
- Routine operations: switching driers, filters, reactor systems, regenerations.
- Remediation of soil/sites

STEP 3: CHECK DATABASES WITH HISTORICAL DATA

The objective is to further refine and complete the inventory, which was drawn up in the previous step. This can be done based on the following data:

- Data from Leak Detection and Repair (LDAR) programs. This allows to confirm potential emission sources, already identified in the previous step, as well as to discover other ones. It also allows to rank the most common emitters or those that emit the largest amounts.
- Data from Industrial Hygiene (IH) monitoring campaigns. These not only assists with identification of potential emission sources, but also identifies tasks to which an increased risk of exposure can be associated. For this purpose, however, quality data is required: besides the measurement results, it is also necessary to have measurement and analysis methods that were used, the circumstances (job description, environmental parameters, duration of sampling, whether or not PPE was used, etc.) under which the measurements were carried out.
  Remark: Historical industrial hygiene data should also be checked to ensure that they are still representative of current working conditions. After all, there is no point in drawing up an improvement plan for an outdated situation. In the same way, attention should be paid when the industrial hygiene data were collected: e.g. during a turnaround, during maintenance or during normal operation.
- We also recommend reviewing the Best Available Technology section on diffusive emissions in the 2016 BREF on Common Waste Water and Waste Gas Treatment[4].

STEP 4: PERFORM ADDITIONAL MONITORING

Where data from LDAR or IH monitoring campaigns are missing or incomplete, it may be necessary to supplement these with additional campaigns. It is recommended to carry out

[4] Common waste water and waste gas Treatment/management systems in the chemical sector BREF (2016). https://eippcb.jrc.ec.europa.eu/reference/common-waste-water-and-waste-gas-treatmentmanagement-systems-chemical-sector-0

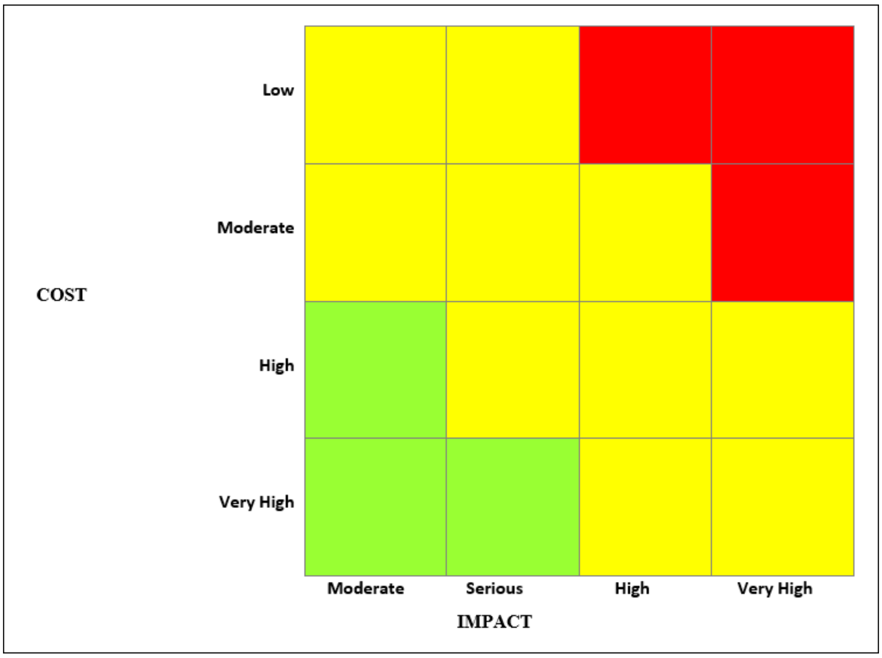
measurements at fixed points as well as personal monitoring in order to identify or confirm both equipment and tasks with an increased risk of exposure. These additional campaigns can be carried out by specialized, accredited labs.

STEP 5: EVALUATE POTENTIAL PROJECTS AND OPERATIONAL MEASURES

Once you have identified the main areas/emission points or tasks where operators can be exposed to higher concentrations than 0.2 ppm or tasks, you need to reflect on changes to the hardware (mostly for high emission points, but possibly also for some task, eg sample taking) or changes in operational procedures (e.g. for maintaining a pump) to ensure that workers are not overexposed to benzene. In chapter 4, potential investment projects are discussed, and in chapter 5 potential operational measures.
This should follow standard procedures of how other projects are studied/handled within the company.

STEP 6: PRIORITISE YOUR IMPROVEMENT PLAN

As a final step, the actions of the improvement plan, identified in the previous steps, should be prioritized. For doing this, one could consider using a priority matrix as shown in the example below. Actions in the red zone (high impact at low cost) will have the highest priority. However, the values of the parameters (low, moderate, serious, high, very high) must be defined individually, company by company and site by site. Remark that actions with a low impact are not considered.



4. Investment projects/hardware changes

As discussed in the previous chapter, once main emissions points and tasks with high exposure have been identified, an inventory of investments that can help to reduce these emissions need to be made.

The following investment should be considered in areas where high concentration of benzene to air is measured or where it is known that relatively high concentrations of benzene are present in the process. The intent of these hardware changes is to minimize air-born quantities of benzene and limit exposure to operating personnel.

Process equipment recommendations to achieve higher cost efficiency:

1. Rotating Equipment:

Pumps:

- Use of dual seals pressurized or unpressurized. The Appendix A Recommended Seal Selection Procedure of the API 682 4th Ed could help to define precisely the selection type.
- Use of sealless pumps (magnetic driven or canned pumps) shall also be evaluated. Special care to contaminants like solids shall be considered for the use of such technology.

Centrifugal Compressors:

- Use of dual dry gas seal tandem type with connection to flare or dual pressurized with a nontoxic barrier gas.

Reciprocating Compressors:

- The compressor shall be equipped with long/long 2 compartment distance piece (Type C of the API 618) or long/short 2 compartment distance piece (type D of the API 618).
- The cylinder pressure packing shall include buffer gas injection, pressure packing combined vent and drain shall be routed to a liquid collection pot connected to flare, outboard distance piece shall be vented and drained to a separate distance piece liquid collection pot. This pot shall be connected to vapor recovery system or flare. Annex I of API 618 give guidelines for distance piece vent, drain and buffer systems.

2. Static Equipment:

Pipelines

- Elimination of screwed couplings and minimization of flanged couplings on piping
- Use of bellows on valves – only in special application (without particles in process fluid)
- Instrumentation with low emissions (for instance remote seal dP cells for level measurement, tapping type of instruments)
- Use welded connections; or redesign to minimize the number of connections (pumps, line corners, valves, etc.), seal welded connections are not preferred

Tanks

- When revamping a tank installing fixed roof tanks
- Dome on external floating roof tanks

- Vapor recovery unit or catalytic oxidation unit for vent streams
- Connect tanks low pressure flare, destruction efficiency of flares could give an issue
- Update any sampling system to minimize exposure.

3. Loading & Unloading facilities

- Use of dry break coupling or minimal leakage couplings
- Vent and purge transfer lines to flare before coupling
- Purge transfer lines back to the original container before coupling
- Purging with nitrogen before uncoupling
- Vapor return system to flare or container

4. Sampling systems

- In-line chromatographs, minimizing manual sampling
- Closed-sampling loops (with pump)
- Self-circulating sampling system (without pump)
- Sample point in enclosure itself so operator not exposed to any fluid
- Vents from sample points to high level and away from other work areas

5. Maintenance areas

- Design for a closed wash out and steam out system with a below or above grade collection / separation drum
- Build enclosed areas for handling parts in maintenance facilities

6. Waste water treatment

- Leak and spill detection at connections
- Intermediate closed waste water tank with skimming and/or steam stripper before send to waste water treatment
- Waste water collection in closed system (for example, not in sewer)

7. Laboratory work

- Hooking up bombs to automated voiding and steam purging unit exhausting to filter unit
- Fume cupboards for analyses
- Laminar flow cabinets for analyses
- Exhausted glove box for analyses

8. Control rooms

- Carefully consider to location of air intake of control rooms or laboratories
- Consider installing active filters at the air inlet

5. Operational and organizational measures + PPE

The following operational, organizational and PPE measures can be considered

1. **Hardware Maintenance related.**
    - Proper maintenance of valves to maintain low emissions from valves; and good fugitive emission program
    - Proper leak testing program of flanges before start-up (commission)

2. **Before working on or inside equipment.**
    - Draining, purging and testing for benzene before opening a system (see also next point)
    - Cleaning vessels with chemicals before entry
    - Camera inspection systems to minimize the need to enter the actual production area and go close to possible fugitive sources
    - Remote tank cleaning
    - Provisions on reactors to dump catalyst and other beds without equipment entry

3. **Further comments on draining, purging and testing for Benzene before opening a system**

The following flowchart may can serve as a starting point for checking what to do and by who during the available for maintenance making of circuits/equipment without entering them.

Note : This flowchart needs to be further developed and It should also be adapted to the specific case of equipment containing (or having contained) streams with > 0,1%(vol) of benzene as it is based on VOC measurement without taking into account the composition of the VOC.

logigrammes mad_EN.xlsx

4. **Influence of the new OEL on the choice of Respiratory Protective Equipment (RPE)**

It should be reminded that the level of protection provided by respiratory protective equipment is expressed by various coefficients corresponding to their airtightness level:

- The nominal protection factor (NPF), calculated on the basis of the total allowable concentration inside the respiratory protective device as set by the respiratory protection standards: NPF = 100 / Total allowable concentration inside (%);
- Assigned protection factor (APF): the expected protection level in real use for 95% of operators trained in the use of respiratory protective devices and correctly using a well-maintained and properly fitted device, after checking.

For a given equipment, the NPF is always higher than the APF. In the absence of a standard specifying the methodology for determining APFs, APFs may differ between two countries for the same equipment.

Remark: The total allowable concentration inside the RPE depends of the OEL: if the actual OEL is reduced from 1 ppm to 0.2 ppm, the total allowable concentration will also have to be reduced by a factor 5.

Some rules regarding RPE selection and use

General rules:

- Prior to the work, it is necessary to identify the substances which may be present and their expected concentrations. If the concentration can evolve it must also be measured during the work. The type of RPE (including choice of filter) will depend on these measures (see table below).
- In the presence of acute toxic chemicals (immediately dangerous to life) such asH_2S, NH3, HF, CO, … or in the case of deficient O_2 it is necessary to wear an independent breathing apparatus (SCBA or air supply).
- In general, wearing RPE is not necessary if the substance concentration is <10% of the OEL, i.e. < 0,02 ppm for Benzene.
- In relation to the discussion of AFP above, measures should be taken to foresee an adequate/proper fit of the RPE for the person wearing the RPE (eg fit testing).

Besides independent breathing apparatus, 3 different types of RPE can be distinguished:

	PFAR: Powered (fan-assisted) respirators Wearing possible if chemical concentration < 60 x OEL In case of VOC, max allowed 500 ppm Is is recommanded to use the PFAR with a combiend filter gaz + dust
	Full face masks (negative pressure) Wearing possible if chemical concentration < 20 x OEL Wear time < 1h
	Half-masks (negative pressure) Wearing possible if chemical concentration < 10 x OEL Wear time < 1h If risks for the eyes, use the full mask.

Type of RPE in function of the Benzene concentration:

				Alarms of gas detectors		Type of PPE depending on concentrations				
Substances	**OEL (8h) ppm**	**OEL (15mn) ppm**	**IDLH ppm**	**Level 1**	**Level 2**	**Breathing apparatus (SCBA, air supply)**	**PFAR powered fan assisted respirator**	**Full face mask with filter(s)**	**half mask with filter(s)**	**Rules**
Benzene (Bz)	1		2000			> 60 ppm	< 60 ppm	< 20 ppm	< 10 ppm	The filters are classified at minimum A2.
Benzene (Bz)	0,2		2000			> 12 ppm	< 12 ppm	< 4 ppm	< 2 ppm	The filters are classified at minimum A2.
VOC				30	100	> 500 ppm	< 500 ppm*	< 500 ppm*	< 10xOEL	The choice of respiratory PPE depends on the presence of Benzene and its concentrations. Filters with at minimum the letters A2. * depending on the Benzene content, the wearing of breathing apparatus may be necessary.

OEL: Occupational exposure limit
LEL: Lower explosivity limit
VOC: Volatil Organic Compounds
Bz and butadiène conc. can be measured with the ULTRA RAE

IDLH: concentration at which exposure is immediately dangerous to life or health
SCBA: Self contained breathing apparatus
PFAR: Powered fan assisted respirator

6 Monitoring

Compliance with an OEL can be assessed by monitoring the level of exposure the workers have been exposed to. This can be achieved by different methodologies, each with levels of uncertainty associated with the data.

Measurement of airborne concentrations of Benzene relate to the potential for exposure by inhalation of benzene vapour at the workplace and is typically compared directly to the OEL.

Measurements of levels of Benzene on the skin relates to the potential for dermal uptake of vapour and liquid in direct contact with the skin. This is out of scope of this document as there is no dermal OEL being set by the EU.

Measurement of levels of Benzene, or metabolites of Benzene, in biological fluids. This indicates the amount of benzene the worker has been effectively exposed to by all routes of exposure (inhalation and dermal) and also includes non-occupational exposure, such as smoking and environmental sources.

Inhalation sampling strategy:
Any sampling must be conducted by trained competent personnel ideally those with occupational/industrial Hygiene experience and qualifications. Guidelines and standards have been developed describing sampling strategies that should be implemented in order to obtain data representative of exposure.
As already mentioned, an EU CEN method exists: EN 689:2018+AC2019-"Workplace exposure. Measurement of exposure by inhalation to chemical agents. Strategy for testing compliance with occupational exposure limit values". It provides instructions on how to test compliance with OELs.

In addition, a group from the “British Occupational Hygiene Society” and the “Nederlandse Vereniging voor Arbeidshygiëne” have produced a guidance document: “Testing Compliance with Occupational Exposure Limits for Airborne Substances”.

According to the CEN standard a similarly exposed worker group (SEG) should be identified and a sampling strategy assigned for each specific worker group or task.

- Following an initial workplace analysis, it is possible to take a minimum of 3 samples for each SEG: If any of the 3 results are greater than the OEL, controls are required to reduce exposure and wherever possible engineering or technical means should be used with PPE being the last resort.
- If all 3 results are less than 1/10 of the OEL then there is a high probability that exposure will not be greater than the OEL and the WG or task are in compliance.
- If 1 or more of the results are greater than 1/10 of the OEL more data needs to be collected to confirm the actual concentration tools such as IH stat can be used to help with understanding and interpreting the data.
- The new EN 689:2018+AC2019 standard allows also to take more samples – but this is of course linked to a higher cost: 4 samples with all 4 results < 15% OEL for getting “green light” or even 5 samples where all 5 have to be < 20% OEL for compliance.
- A statistical approach is also indicated where at least 6 samples must be taken for each SEG. In this case less than 5% of exposure with 70% of confidence, should exceed the OEL.
- In all instances periodic reassessments should be carried out to confirm no changes to exposure have occurred.

In some member states, the application of the EN689 standard is imposed or strongly advised or – in France – is the local regulation inspired on its previous version EN689:1995.

<u>Measurement of airborne concentrations of Benzene.</u>

Full or partial shift monitoring:

Measurement of Benzene levels in the workers breathing zone can be assessed by collecting Benzene vapour onto suitable media followed by desorption and analysis via Gas Chromatography. With an OEL of 0,2 ppm, the monitoring methodology should have a limit of quantification (LOQ) of at least $1/10^{th}$ of the OEL, i.e. 0,02 ppm or 0.065 mg/m^3.
Benzene sampling can be carried out either using a passive or active sampling approach.
A passive sampling approach uses a device containing sampling media which has a known diffusion coefficient for Benzene, and if worn in the breathing zone for a sufficient length of time, can represent the potential airborne concentration the worker is exposed to. After sampling, the media is placed in a sealed container and sent for analysis. This type of sampler is good for assessing full shift exposure and is easy to set up and affix to the worker.
The type of media will have a specified “uptake rate” provided by the supplier. Knowing the uptake rate, the duration of exposure and the mass of contaminant, a concentration (ppm or mg/m3) can be calculated and comparted to the OEL.

An active sampling approach assesses airborne concentrations of benzene using a personal sampling pump and suitable media (“pump and tube”). A pump calibrated against a certified flow measuring device is used to draw air through the sample media which is placed in the breathing zone of the worker. The maximum flow rate, minimum and maximum sampled volumes are stated in the method or by the laboratory. After sampling the media is placed in a sealed container and sent for analysis. The duration of sampling and the flow rate will together determine the volume sampled, analysis will determine the mass of Benzene on the media and a mass/volume concentration can be determined. In the context of a decreasing OEL for benzene, sample duration as well as flow rate should be maximised as much as practically feasible in order to obtain the best sensitivity and to approach the technically best possible detection and quantification limits for this method.

Task specific monitoring (Short term):
Passive samples are typically not used for short term tasks. Short term tasks can be assessed using active sampling methods, but it is imperative that sufficient volume is sampled to enable a concentration to be calculated which is sufficiently lower than the OEL to provide information on compliance. This will relate directly to the limit of detection/quantification of the analytical method. To confer compliance, it is good practice to confirm exposure is less than 1/10 of the OEL.

E.g. required limit of detection calculation for short term sampling.
OEL = 0.2ppm for Benzene = 0.65 mg/m3 = 0.65 µg/litre

Assume a 15 minute task sample is monitored
Flow rate = 200ml/min
Total volume = 3litres

The analytical method would need to be able to measure 1.95 µg on the media at the OEL.
At 1/10 OEL this would be 0.195 µg.

(Mass on media for 3 litre sample = (0.65 µg/litre x 3 litres air sample)/1 = 1.95 µg)

Therefore, the analytical method must be capable of detecting 0.195 µg on the sampling media.

The retained benzene is extracted for analysis by thermal desorption or chemical desorption with CS_2 followed by analysis via Gas Chromatography with a suitable detector to identify the benzene component in the sample. Enhanced sensitivity can be found by using a Thermal desorption sampler (this increases the amount of airborne chemical sent to the instrument for analysis). Another method of enhancing sensitivity can be obtained by using mass selective detectors. The laboratory specified will be able to provide specific information on capability.

Direct measurement of airborne concentrations of Benzene:

There are instrumental methods and colourimetric tubes that can indicate the concentration of Benzene at a specific time and location. Both of these methods are liable to cross contamination from other hydrocarbons.

Colourimetric tubes; there are several manufacturers that produce tubes that change colour when air contaminated with Benzene is drawn through them. A specific volume of air is “drawn” through the tube using a hand pump or specific electrical pump. The material inside the tubes changes colour when it reacts with benzene. The concentration is indicated on the tube. The detection range is related to the tube and the Volume sampled (number of pumps) e.g 0.1ppm – 40ppm. As can be seen in this example the lower end of the concentration range is ½ of the proposed OEL. To increase sensitivity more volume would need to be sampled, with the risk of cross contamination from other hydrocarbons present. Under development are opto-electronic analysers that “read” single-use product-specific tubes. The objective is that detection limits from 1 ppb on can be achieved.

Direct measurement instruments: the method used is a photo ionisation detector. A photo ionisation detector (PID) is not specific and will detect, with differing levels of response, any molecule that can be ionised by the energy of the UV lamp. To overcome this and be specific to Benzene several manufacturers have developed Benzene specific instruments. All of these use a PID and in addition use a prefilter “scrubbing” tube, the tube is intended to remove all Hydrocarbons other than Benzene. The resolution of such instruments is 0.01ppm. Calibration is usually made with a 5ppm standard, as such the resolution at 0.01 ppm will have some uncertainty associated with it. At the current time, all such instruments meet the requirements for use in a flammable area (ATEX).
A recent development is the combination of a portable PID with a micro GC. This allows an effective quantification limit of 50 to 100 ppb and first tests shows potential for a rapid assessment in non ATEX areas.

Biological monitoring for Benzene:

Biological monitoring is a way of assessing chemical exposures by measuring the chemical or its breakdown products (metabolites) in a biological sample, usually urine, blood or breath. Biological monitoring is particularly useful to evaluate worker exposure where chemicals can be significantly absorbed through other exposure paths such as the skin, and where controls rely upon the use of personal protective equipment, such as gloves and masks. Biological monitoring can evaluate the total dose the workers are exposed to from inhalation and skin exposure.

Currently no Biological Limit Value (equivalent to an 8 hour exposure at the workplace limit) has been proposed by the Advisory Committee on Safety and Health at Work (ACSH) under CMD, although the ACSH agrees on the principle of the usefulness of biomonitoring for benzene.

Benzene exposure produces multiple metabolites with potential for biological monitoring. They vary in usefulness for occupational monitoring depending on the amount of exposure. Among available metabolites for exposure assessment, S-phenylmercapturic acid (SPMA)in a urine sample from exposed workers provides good sensitivity and specificity at exposures

of 0,2 ppm or less and has established correlations to air benzene concentration that can support exposure monitoring.
Sometimes, urinary benzene is measured too as it is very specific and very sensitive method, but there is currently no existing reference value for the workplace.
In the past, the metabolite *trans, trans*-muconic acid (TTMA) was often measured due to its ease of application and lower cost. However, at benzene exposures of 0,2 ppm or less its specificity is low due to confounding factors. Use of TTMA for biological monitoring is not recommended anymore in the context of the new lowered Benzene OEL.
Important remark: Biomonitoring does not distinguish between sources of exposure, thus levels of uncertainty must be taken into account due to Benzene exposure from smoking or other environmental sources, such as car interiors, parking lots and gas stations.

CONCLUSIONS

The objective of this note is to provide some guidance to refinery and petrochemical sites to develop a plan for implementation of an OEL for benzene of 0.2 ppm, a limit that will most likely be binding as of first half of 2025.
Different steps in developing this plan, consisting of investments and operational measures/changing + adequate use of RPE is described. Also, information is given on how to monitor exposure to benzene.
This document is a living document and will be updated based on feedback and input of members.