United States Environmental Protection Agency
Research and Development

Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

EPA/600/S7-86/007 May 1986

EPA

# Project Summary

# Environmental Assessment: Source Test and Evaluation Report Addendum — Lurgi-Type Medium-Btu Gasification

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**This report is an addendum to "Environmental Assessment: Source Test and Evaluation Report-Lurgi Type (Kosovo, Yugoslavia) Medium-Btu Gasification, Final Report," EPA-600/7-81-142, August 1981. It contains analytical data on 21 gasification plant streams, not included in the original report.**

**Condensable organics from the plant's major gas, solid-phase, and selected liquid-phase streams were characterized by the EPA protocol for a Level 1 source assessment to determine the mass distribution of chemical classes which they contained. GC-MS analyses were performed on gas stream condensates to quantify their levels of hazardous PNAs. Profiles of the sulfur- and nitrogen-bearing species in these condensates were obtained with element-specific GC detectors.**

***This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in two separate volumes of the same title (see project Report ordering information at back).***

## Introduction

Coal, because of its abundance, is a potential replacement for depleting U.S. petroleum reserves and may eventually become a principal source of hydrocarbon fuels and chemical feedstocks. Consequently, substantial efforts have been devoted to evaluating coal utilization technologies for their economic and environmental performances. Among the leaders in the rapidly developing technology for converting coal to clean fuel is steam/oxidant gasification.

The purpose of this study was to obtain, from a commercial facility, data that could be used in an environmentally based evaluation of Lurgi-type technology. The test facility, in the Kosovo region of Yugoslavia, uses 3.4 m pressurized gasifiers to convert lignite to medium-Btu gas. The study, sponsored by the U.S. EPA, was conducted over a period of several years as a cooperative effort among scientists from the U.S. and Yugoslavia. The four-phase program investigated several aspects of plant-related environmental contamination including: source discharges, fugitive emissions, and ambient air pollution. Results from each of these programs have been reported separately. However, during Phase II of the Source Test, samples of process liquids and gas stream condensates were collected which were not analyzed in time for the results to be included in the Phase II report (EPA-600/7-81-142). These analyses have been completed, and the results are the subject of an addendum to the Phase II report. The addendum provides information on the mass distribution of chemical classes in the condensable organics from the plant's significant discharge streams. It also provides information on specific polycyclic aromatics and on the distribution of heteroaromatic hydrocarbons containing nitrogen and/or sulfur.

For data obtained from the study to be properly interpreted, it must be recognized that the Kosovo plant does not include all of the design and operating features of modern Lurgi-type facilities. For example, the Kosovo plant does not employ many of the pollution control processes that will be incorporated in U.S. gasification facilities. Therefore, many of the "uncontrolled" discharges from the Kosovo plant are not representative of the "controlled" discharges which are expected from future U.S. plants based on similar technology. However, the Kosovo plant's uncontrolled discharge streams characterized in this program are expected to be similar in composition and relative flow rates to analogous internal streams in future U.S. plants (unless specific design or operational features for these plants cause significant differences). Therefore, the compositions of the uncontrolled discharge streams at Kosovo will be, in many cases, representative of the inlet streams to pollution control processed in future U.S. plants based on similar technology. Within these constraints, the data obtained in this study can be used to:

- Indicate the nature of the organics found in uncontrolled discharges from the processing units of a gasification plant based on similar technology. (Most of these streams are expected to be routed to pollution control units in future U.S. plants.)
- Assess the need for pollution control processes for potential discharge streams from future U.S. plants based on similar technology.
- Indicate the nature of the organics that may be present at low levels in the discharges from pollution control devices.

## Plant Description

The Kosovo coal gasification plant is an integral part of a large minemouth industrial complex that includes a coal mine, a coal preparation plant, a coal gasification plant, an air separation plant, an ammonia-based fertilizer plant, a power generating plant, and a steam generating plant.

The gasification facility, hereafter called the "gasification plant," consists of nine unit-operations as shown in Figure 1. The gasification plant consumes dried lignite and produces two primary products: a medium-Btu fuel gas having a net heating value of about 14 MJ/m (360 Btu-scf) at 25 °C (77 °F), and hydrogen which is used as an ammonia synthesis feedstock. Also produced are four liquid by-products: crude phenol, tar, medium oil, and naphtha. The plant's operation is explained below.

Upgraded coal from the Kosovo mine is dried in autoclaves (Fleissner process) to reduce the moisture content from about 50 to 20 percent and then sized to select particles ranging from 6 to 60 mm. After being sized, the dried coal is reacted with oxygen and steam in Lugi-type gasifiers at 2.5 MPa (25 atm) pressure to produce gas which is quenched, cooled, and then cleaned by the Rectisol process prior to its transport to the utilization site for use as fuel or as feedstock for ammonia production. As the hot gas is quenched and cooled, condensable organics are removed with the quench liquor and hot gas condensate, after which acid gases ($H_2S$ and $CO_2$) are removed by sorption with cold methanol. The methanol, rich in acid gas, is regenerated by staged depressurizing and heating, releasing a $CO_2$-rich gas (which is vented to the atmosphere) and an $H_2S$-rich gas (which is routed to a flare). The condensable organics in the quench liquor and hot gas condensate are separated by decantation into a series of

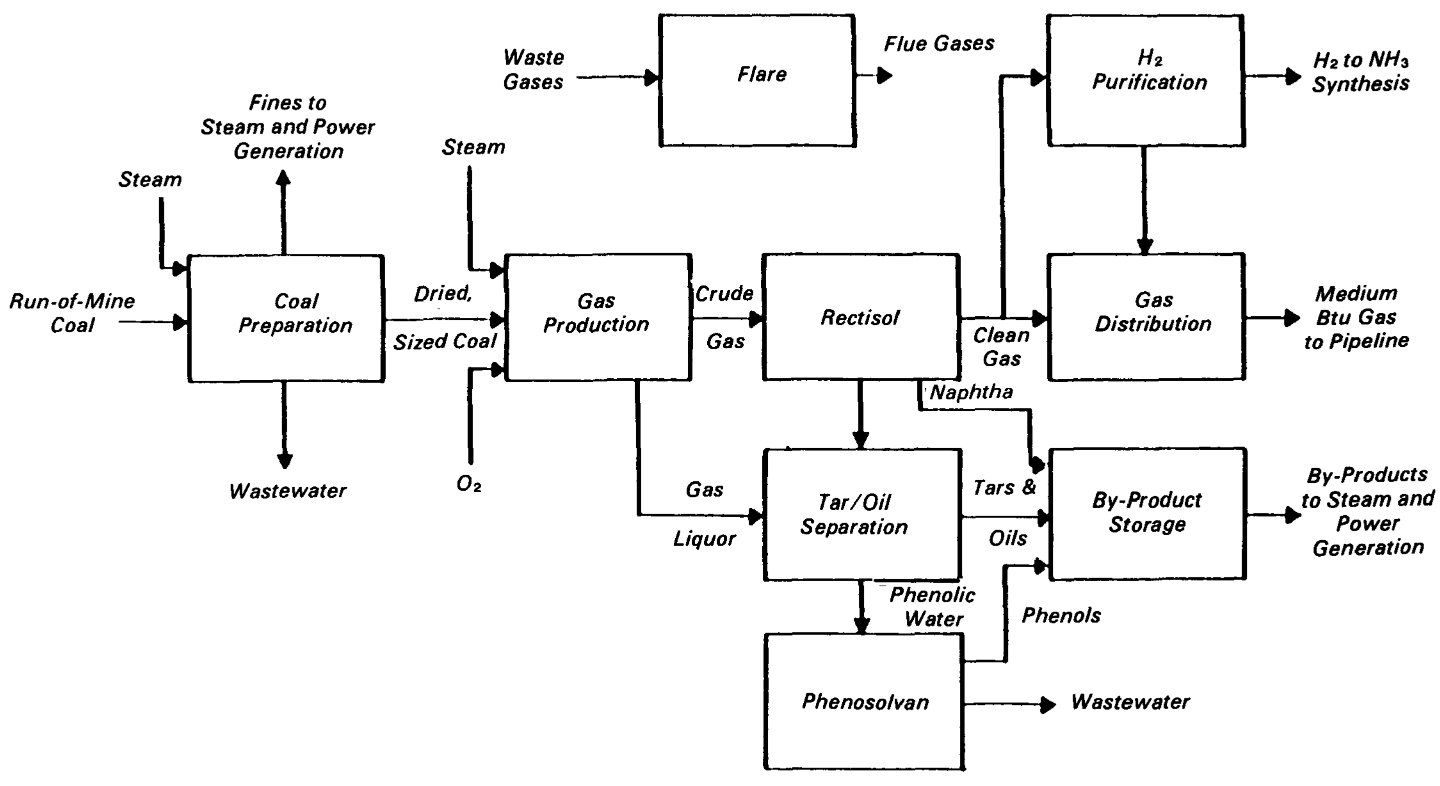


*Figure 1. Simplified flow diagram of the Kosovo coal preparation/gasification plant operations.*

fractions: heavy tar, tar, medium oil, and naptha. The residual waters are combined, stripped to remove ammonia, then extracted with diisopropyl ether to remove organics (crude phenol), and finally discharged.

## Experimental Approach

A primary objective of Phase II testing was to characterize the trace organics that are being transported by the plant's discharge streams as aerosols and vapors. The 21 streams, selected for sampling, provided a representative cross-section of the Kosovo facility. Their selection was based on a high discharge rate and/or a potential source of organics. EPA methods, modified when needed to satisfy sample or stream conditions, were used to collect condensable organics from gaseous streams. The organics were collected by a train consisting of: an entrainment separator, an ice-cooled condenser, and a resin-filled absorber, in series.

Conventional grab sampling was used for liquids; grab and composite sampling, for solids. Samples were refrigerated during both transport and the storage period between collection and analysis. Sorbed vapor samples were recovered from their collection resin by Soxhlet extraction with methylene chloride and combined with the organic extracts of their streams' condensate prior to analyses.

Sample characterization consisted of a combination of the following methods:

- EPA's protocol for Level I Source Assessment using:
  - GC-FID to determine volatile organics
  - Gravimetric analysis to determine nonvolatile organics
  - Liquid chromatography to fractionate mixtures according to polarity/chemical class,
- GC-MS with a liquid crystal GC colum to identify and quantify selected polynuclear aromatics, and
- Gas chromatography with a selected detector to obtain stream profiles of heteroatomic species containing nitrogen and sulfur.

The streams sampled and the analyses performed are summarized in Table 1.

## Test Results

The Kosovo trace organics study provides the following information:

- Concentration and mass flow data for condensable organics in gasification plant discharge streams,
- Comparisons for quality control,
- Composition data of the various types of organics transported by these streams, and
- Levels of selected polynuclear aromatics transported by gasification plant streams.

### *Organic Concentrations and Mass Flow*

The concentrations and mass flow of condensable organics are summarized in the report for the gasification plant's 10 gaseous streams: the start-up vent, ammonia stripper vent, phenolic water tank vent, HP and LP coal lock vents, $H_2S$- and $CO_2$-rich waste gases, tar separation waste gas, medium-oil tank vent, and naphtha tank vent. The concentrations range from 14 mg/m$^3$ to 125 g/m$^3$; and the mass flows, from 8 g/hr to 120 kg/hr. The start-up vent and the ammonia stripper vent, when operating, transport most of the condensable organics. However, the start-up vent discharge changes from

***Table 1.*** *Analyses Performed on Kosovo Gas Stream Condensates, Process Liquid, and Solid Wastes*

| | Analyses | | | | | | |
|---|---|---|---|---|---|---|---|
| *Stream* | *Particulate Determination* | *TCO* | *Grav* | *LC* | *GC Sulfur* | *GC Nitrogen* | *GC-MS PNAs* |
| Gas Stream | | | | | | | |
| *Fleissner Autoclave Vent* | x | x | x | x | | | |
| *Low Pressure (LP) Coal Lock Vent* | x | x | x | x | x | x | x |
| *High Pressure (HP) Coal Lock Vent* | x | x | x | x | x | x | |
| *Start-up Vent* | x | x | x | x | | | x |
| *$H_2S$-Rich Waste Gas* | | x | x | x | | x | x |
| *$CO_2$-Rich Waste Gas* | | x | x | | | | x |
| *Crude Product Gas* | | x | x | | | x | |
| *Tar Tank Vent* | | x | x | x | | x | x |
| *Medium-Oil Tank Vent* | | x | x | x | | x | x |
| *Tar Separation Waste Gas* | x | x | x | x | | x | |
| *Phenolic Water Tank Vent* | | x | x | x | | x | x |
| *Ammonia Stripper Vent* | | x | x | x | x | x | x |
| *Naphtha Storage Tank Vent* | | x | x | x | | | x |
| *Waste Gases to Flare* | x | x | x | | | | |
| Other Streams | | | | | | | |
| *Fleissner Condensate* | | | x | | | | |
| *Gasifier Ash* | | | x | | | | |
| *Heavy Tar* | x | x | x | | | | |
| *Phenolic Water* | x | x | x | | ⊕ | ⊕ | ⊕ |
| *Tar* | | x | x | x | ⊕ | ⊕ | ⊕ |
| *Medium Oil* | | x | x | x | + | + | ⊕ |
| *Naphtha* | | x | | | ⊕ | | ⊕ |

*x — analyzed in Yugoslavia.*
*+ — analyzed in U.S. using random grab samples.*
*⊕ — Data not included in this report but included in EPA-600/7-81-142.*

combustion gas to product gas over a start-up period; and the values shown may represent a worst case. On the other hand, the mass flow value of the ammonia stripper vent is based on a flow with one gasifier in continuous operation.

The phenolic water tank discharge contains the highest concentration of organics but, because of its smaller volume, its mass flow is comparable to those of the coal lock vent and the $H_2S$-rich waste gas stream.

Total organic (TO) concentrations were determined as the sum of volatile (VOs) and nonvolatile organics (NVOs). VOs were determined chromatographically, while NVOs were determined gravimetrically.

Although the major emphasis of this addendum was on gas stream condensates, organics from other streams (e.g., process liquids and solid wastes) were included in the test results. However, aqueous effluent from the Phenosolvan extraction process could not be obtained at the time of testing so a total organics measurement by the test protocol is not included in the addendum.

## Quality Control Comparisons

Comparisons made between these values and relatable data from other determinations and other gasifiers supported the validity of these results. Comparisons made were:

- VO concentration with light aromatics determined on the same stream during Kosovo Phase II testing,
- NVO concentration with tar and oil as obtained from the particulate determination on the same stream, and
- Kosovo organics (VO and NVO) with some values from Wellman-Galusha (Ft. Snelling), Chapman (Holston), and Riley Products (Worcester) gasifiers.

## Composition of Kosovo Organics

The distribution profile of Kosovo organics as indicated by column chromatography on silica gel is shown in Figure 2. Percentages indicated are based on the mass eluted from the column so that the sum for each stream totaled 100%. The large portion of eluent found in Fraction 1 of several streams suggested that the aromatics eluted early. This and other anomalies are addressed in the parent report. Concentrations of organics in each fraction and in the sample stream are shown in Table 2. All data expressed as milligrams per cubic meter represent stream concentration. LC fraction numbers coincide with those shown in Figure 2.

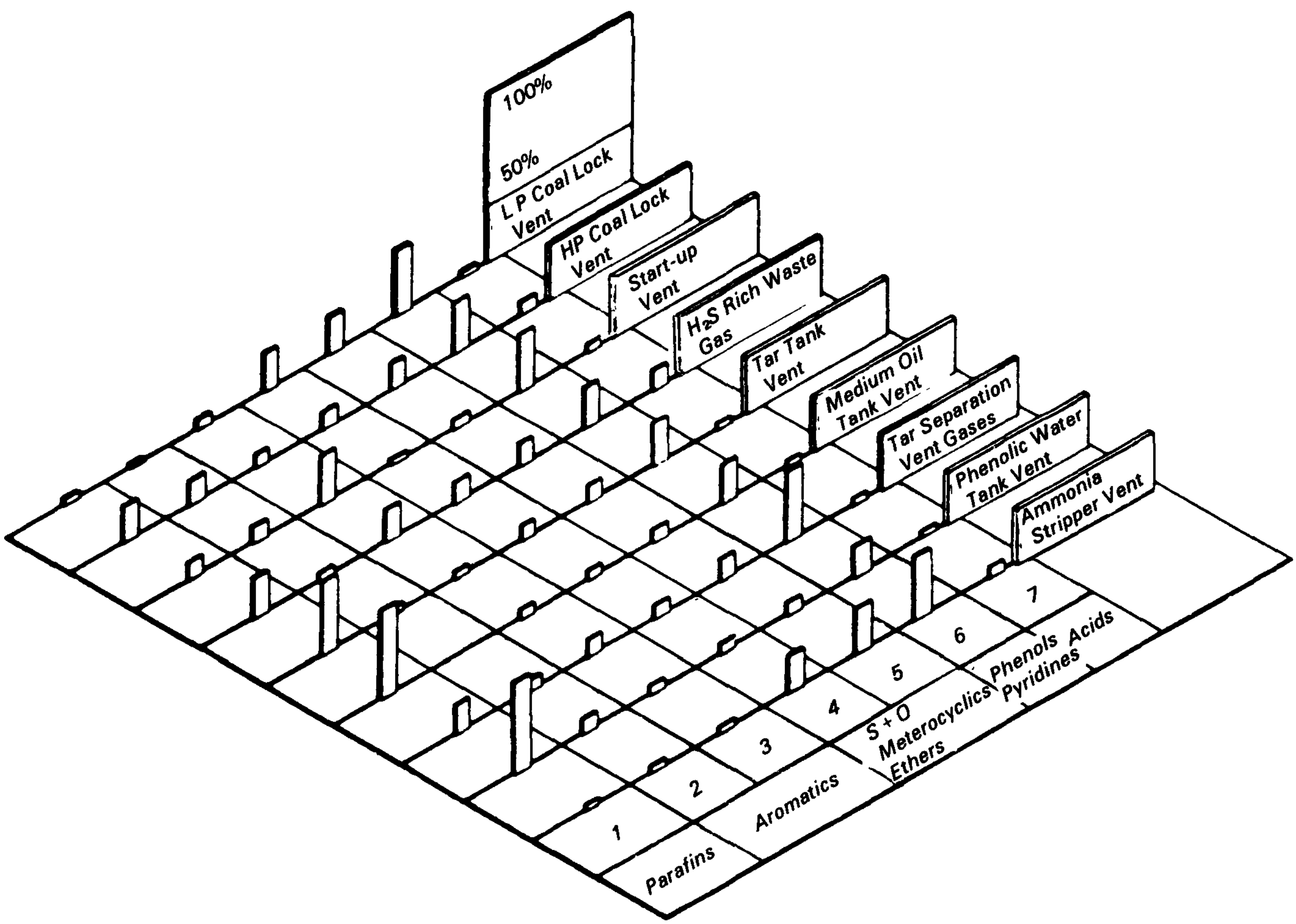


*Figure 2. Distribution of chemical classes across the LC fractions of Kosovo gas stream condensates.*

*Table 2. Concentrations of Organics Found in Each Liquid Chromatographic Fraction and in the Sample Stream*

| Source | LC Fraction, mg/m³ 1 | 2 | 3 | 4 | 5 | 6 | 7 | Total Recovered mg/m³ | Concentration In Stream mg/m³ |
|---|---|---|---|---|---|---|---|---|---|
| Fleissner autoclave Vent* | 229 | 47 | 80 | 47 | 73 | 203 | 20 | 699 | 1,114 |
| LP Coal Lock Vent | 167 | 79 | 426 | 1,456 | 1,281 | 2,297 | 266 | 5,981 | 7,739 |
| HP Coal Lock Vent* | 395 | 285 | 145 | 168 | 282 | 563 | 67 | 1,912 | 2,872 |
| Start-up Vent* | 458 | 430 | 1,743 | 160 | 268 | 1,595 | 302 | 4,956 | 5,540 |
| $H_2S$-Rich Waste Gas | 19 | 5 | 12 | 7 | 8 | 18 | 4 | 73 | 130 |
| Tar Tank Vent | 3,734 | 449 | 410 | 652 | 753 | 2,179 | 225 | 8,402 | 14,412 |
| Medium-Oil Tank Vent | 2,275 | 229 | 246 | 250 | 335 | 1,061 | 76 | 4,471 | 21,118 |
| Tar Separation Waste Gas* | 266 | 105 | 154 | 129 | 183 | 649 | 38 | 1,525 | 3,302 |
| Phenolic Water Tank Vent | 32,190 | 3,335 | 2,458 | 3,650 | 4,185 | 10,847 | 857 | 51,737 | 124,884 |
| Ammonia Stripper Vent | 1,880 | 2,607 | 2,222 | 16,923 | 17,692 | 27,949 | 4,145 | 73,419 | 99,218 |
| Naphtha Storage Tank Vent | 342 | 25 | 40 | 44 | 34 | 380 | 37 | 902 | 5,589 |

*All values computed to stream concentration and expressed as milligrams per normal cubic meter of gas.*
**The concentration values for this stream were corrected for a procedural error that involved an unequally divided sample.*

Results from the characterization of process liquids and solid wastes by the Level 1 procedure show that both phenolic water and Fleissner condensate contain about 10 g of organics per liter; gasifier ash contains virtually no extractable organics; and heavy tar, consisting of about 85% extractable organics, contains a relatively high (53%) volatile content. Results from silica gel chromatography show that tar, heavy tar, medium oil, and phenolic water have similar distribution profiles.

## Infrared

The infrared spectra of samples and fractions from this study are not representative of the condensable organics from the streams of origin: only the very high boiling material is represented. Although these spectra show evidence of contamination, they provide useful information about the structure of the samples' heavy ends.

## Gas Chromatography for Nitrogen- and Sulfur-Containing Species

Gas chromatograms of nitrogeneous species in samples from four streams (HP and LP coal lock vents, tar separation waste gas, and tar tank vent) were very similar; those from three other streams (ammonia stripper vent, phenolic water tank vent, and medium oil tank vent) were dissimilar. The dissimilar streams showed different mixtures of unidentified compounds. Chromatograms of sulfur species also show many differences among streams. Some differences relate to the types of components; others, to the relative component quantities.

Insight into the complexity of these heteroatomic species is provided by nitrogen- and sulfur-specific chromatograms of medium-oil fractions. Chromatograms of acid extractables, base extractables, neutrals, a reconstituted acid-precipitate, head space vapor, steam distillate, and still-pot water indicate the wide range of nitrogen and sulfur compound classes found in Kosovo condensate.

Chromatograms illustrate the range of compounds in the acid, base, and neutral fractions. Compounds shown on the chromatograms represent proton donors, proton acceptors, and neutrals. Some compounds in each class contain nitrogen; some, sulfur; and some, probably both. Classes present could include: pyridines, cyanophenols, hydroxypyridines, pyridylmercaptans, diazines, pyridazines, nitriles, thiazoles, and oxazoles, as well as the complete distribution of aliphatic and paraffinic hydrocarbons.

## Polynuclear Aromatics

The concentrations of selected polynuclear aromatics (PNAs) in Kosovo condensates are shown in Table 3. Although all concentration values were obtained by GC-MS, different levels of detectability were achieved because of dilution effects. All measurements were made to a sensitivity of 0.1 ppm in the extract on which the GC-MS measurement was performed. The concentration of BaP in the LP coal lock condensate (670 μg/m³) was in close agreement with the estimated value (500 μg/m³) that was reported in the Phase II report. The estimate was based on the level of tar/oil in the particulate aerosol collection and the concentration of BaP in medium oil.

*Table 3. Concentrations of Selected Polynuclear Aromatics in Kosovo Gaseous Discharge Streams*

| Source | Concentration, μg/m³ BaA | BaP | dBahA | BhF |
|---|---|---|---|---|
| LP Coal Lock Vent | 163 | 670 | 52 | 670 |
| Ammonia Stripper Vent | 85 | 20 | <2.1 | 12 |
| Naphtha Storage Tank Vent | <0.06 | 0.085 | 0.06 | 0.11 |
| Start-up Vent | — | 139 | <2.1 | — |
| Tar Tank Vent | — | 252 | <10 | — |
| Phenolic Water Tank Vent | — | <50 | <50 | — |
| Medium-Oil Tank Vent | — | <6.5 | <6.5 | — |
| $H_2S$-Rich Waste Gas | — | <0.6 | <0.6 | — |
| $CO_2$-Rich Waste Gas | — | <0.7 | <0.7 | — |

*All (<) values are calculated from a minimum detectable concentration of 0.1 ppm in the measuring solution.*

*— Not determined.*

*BaA — Benzo(a)anthracene*
*BaP — Benzo(a)pyrene*
*dBahA — dibenz(ah)anthracene*
*BhF — Benzo(h)fluoranthene*



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