1 MS-200 ACCESSORIES-Sensitivity Enhancement Using a Trap Evacuate Desorb (TED) Interface[1]

1.1 Summary

Despite the high sensitivity and low detection limits of the MS-200 for a vast range of aromatics, chlorinated and other volatile organic compounds, there are applications that could benefit from a higher sensitivity. Therefore Kore offers the TED interface as a means of achieving further pre-concentration to the membrane inlet system in order to improve the detection limit for many components from the low ppb levels, into the mid to low ppt levels.

Sensitivity enhancements are typically achieved using pre-concentration of chemicals onto an adsorbent. The uniqueness of the TED method is that the adsorbent material is evacuated to a pressure of about 1 mbar, before heating the trap material to desorb the analyte. Removing about 99.9 % of the background air, before desorbing, results in a second enrichment of the sample relative to the background air. In addition to high sensitivity enhancement the TED also shows some advantages in handling high humidity samples, which can cause problems with the spectrometer vacuum.

The basic working principles of the trap evacuate desorb interface (TED) and performance in comparison to the standard MS-200 membrane interface are described in this note.

1.2 Introduction

The standard MS-200 uses a double membrane pre-concentrator as a sample inlet to the mass analyser. This inlet system is very suitable for the analysis of aromatic and chlorinated hydrocarbons and other selected volatile organic compounds (VOCs) for which analysis can be performed semi-continuously down to low ppb levels. However the sensitivity of the measurement depends on the ability of a component to permeate through the membranes which in the case of polar or oily components limits the detection to ppm levels .

A standard sample pre-concentration method is to use an adsorption trap. An ideal adsorption trap will selectively collect traces of VOCs from a sample stream that is passed through the trap, but will not collect any of the major compounds in air. In this way the trap material will filter out and hold onto traces of VOCs, building up sufficient quantity of trace contaminants to allow later analysis. A common method to remove the VOCs is to heat the trap material, releasing the analyte into a gas stream to be analysed.

[1] The TED interface was patented by Kore Technology in 2002.

The Trap-Evacuate-Desorb (TED) thermally desorbs the trap at a lower than ambient pressure, which increases the concentrating effect of the trap. Evacuating the trap to 1 mbar before desorption, rather than desorbing at atmospheric pressure (1013 mbar) results theoretically in a further concentration factor of 1013, relative to air (mainly N_2 and O_2) molecules. The standard membrane concentrator of the MS-200 results in an enrichment of benzene at a factor of around 100 per membrane.

This TED method is particularly suitable as a retrofit to the standard membrane inlet of the MS-200, which uses a pressure step down to 1 mbar across a first membrane, before a final pressure step across the second membrane into the ultra high vacuum of the analyser chamber.

1.3 The Desorption Interface

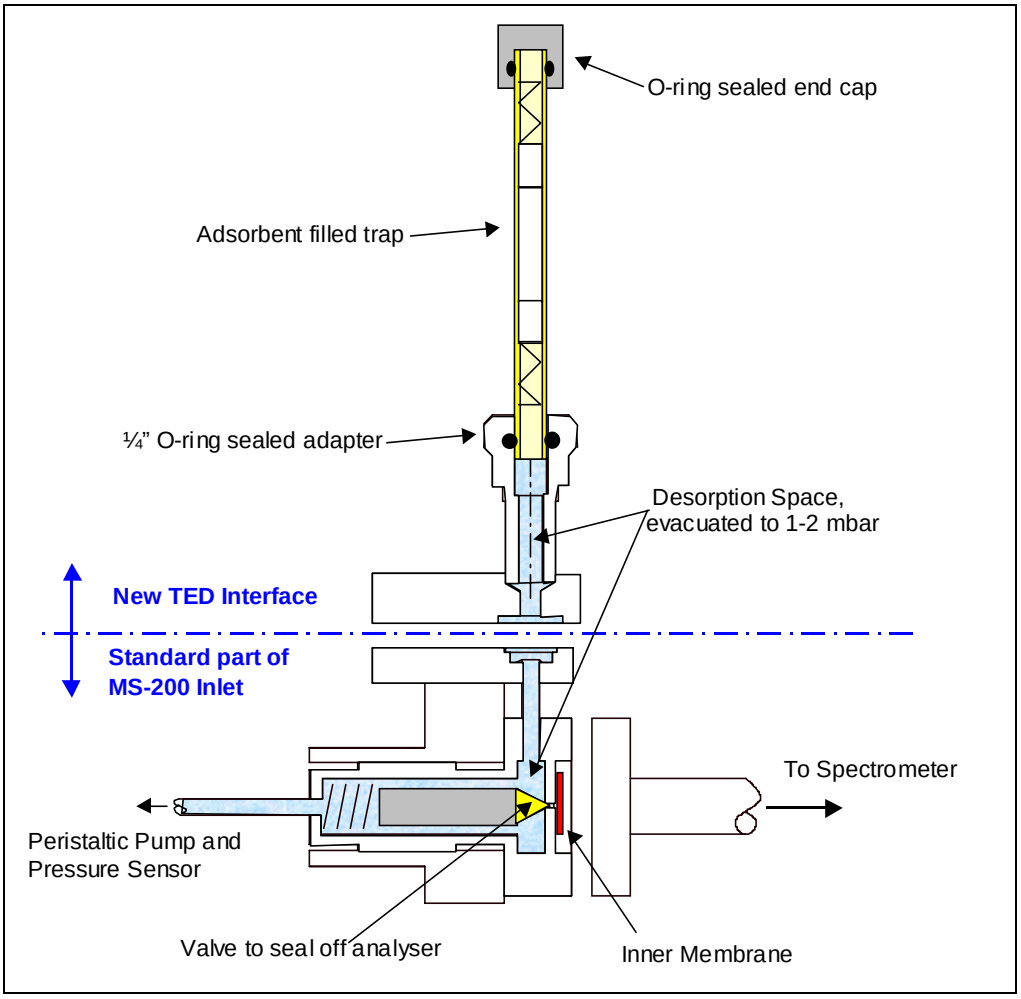

Figure 1: Outline of the MS-200 TED Option

The TED accessory is shown in Figure 1. The TED interface replaces the standard outer membrane holder and outer membrane so that the adsorption tubes can be fitted. This

interface allows sealing of the adsorption tube, and the evacuation of the air from the space created between the adsorption trap and the inner membrane of the analyser. Evacuation of the desorption space is done using the peristaltic pump, normally used to evacuate the pressure step between the outer and the inner membrane in the double membrane configuration of the MS-200. This way the trapped VOCs are desorbed into a vacuum of about 1 to 2 mbar before permeating through the inner membrane into the ultra high vacuum (UHV) of the analyser chamber.

1.3.1 The desorption oven

To allow thermal desorption, using the desorption interface described above, a micro-furnace, or desorption oven fits around the adsorption trap and includes the heater and temperature sensor. This desorption oven is shown in Figure 2

Heating is achieved by applying a voltage to a nickel wire, supported in a cylinder of a high temperature ceramic. A thermocouple is placed inside the heater, on a location where temperature reading is representative of the temperature inside the trap material.

The heater is tailored to suit the commonly used glass or stainless steel adsorption tubes of 6.35mm diameter and 90mm length. By sliding the tubes into the heater, tubes can be changed quickly and easily.

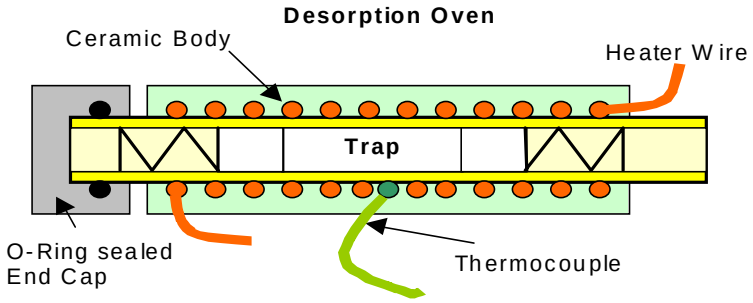

Figure 2 The desorption oven

The oven is capable of heating the adsorption tube to a temperature of 450°C.

The temperature of the heater is controlled using a commercial available temperature controller together with a 24V switch-mode power supply and a power regulator. The controller is programmable to change the temperature in a slow ramp, or to perform a step change of temperature.

In order to speed up the cooling of the tube, a fan cooler is installed next to the heater and is switched on and off from the controller.

At full power, the heater requires about 60 seconds to follow a step change of the controller from 30°C to 200°C. The temperature of the adsorbent is measured with a thermocouple introduced into the centre of the adsorbent material.

1.4 The Adsorbent Material

An ideal adsorption trap will selectively collect traces of VOCs from a sample, but will not collect any of the major compounds in the air. Adsorption traps contain resins with a large surface area to volume ratio, with a high affinity to selectively adsorb chemicals that are passed through them. Different trap materials have differences in their affinity for lighter or heavier VOCs (i.e. larger or smaller numbers of carbon atoms in the molecule). Affinity of an adsorbent to a VOC or other chemical to be collected is typically described by means of the break-through volume. The break-through volume is defined as the volume of carrier gas that will purge an analyte through one gram of adsorbent resin in a desorption tube at a specific temperature. This means that once the break through volume of an adsorption trap is reached, the collected VOCs will leak out of the exit of the tube. The break through volume is highly temperature dependent, and decreases with increasing temperature

Therefore the optimum trap material has break through volumes for the range of VOCs to be analysed that are sufficiently high to be able to collect as much material onto the trap as is needed to perform a meaningful analysis. For the TED, typically, a versatile adsorbent called Tenax TA® (Tenax) is used. It is a porous polymer resin and was specially designed for the trapping of volatiles and semi-volatiles in gaseous form. Tenax has a low affinity for nitrogen and water, which allows the removal of water from the sample prior to analysis.

1.5 Adsorption Tubes

The adsorbent tubes used are silicate glass tubes with an external diameter of 6.35mm, internal diameter of 4mm and a length of 90mm. These tubes are filled with approximately 125mm^3 of Tenax TA® (around 31mg of material). The adsorption material is held in place with a plug of glass wool on either end. Additionally a retaining spring made of nickel wire is introduced to retain the glass wool to avoid loosing the packing when sudden changes in pressure occur. A schematic of the tubes can be seen in Figure 3.

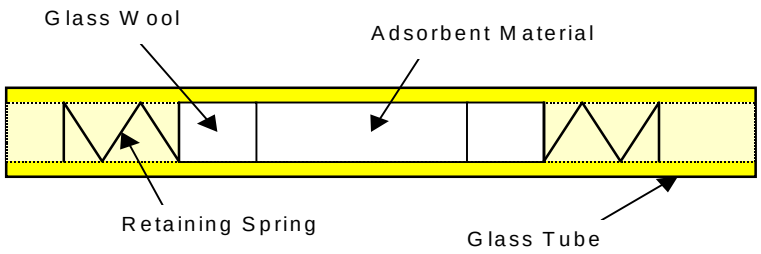

Figure 3 Schematic of the Adsorption Tube

1.6 Cleaning the Adsorbent Tube

Prior to use, the adsorbent in the adsorbent tube has to be cleaned to remove all traces of adsorbed matter from previous experiments. To achieve this the tube is fitted into the desorption oven and heated to 250°C. A flow of 200ml/min of dry nitrogen is passed through the tube. At this temperature the break through volume for, for example, benzene is reduced from 70litre at 20°C to 0.001 litre per gram of adsorbent. As the trap used contains about 31mg of adsorbent resin, this relates to a break through volume of 0.31µl of nitrogen. Purging the tube for five minutes, (1000ml of air) is sufficient to clean out benzene and most of the higher boiling point components. It has been confirmed that cleaning tubes between experiments using this procedure is sufficient to reduce the background to an insignificant level.

For initial conditioning of the adsorbent material, typically the tube is purged with 10 to 50ml/min of high purity (less than 1ppm oxygen) gas. Then after 10 minutes, the trap temperature is increased at a rate of 4 to 10°/min to approximately 25 to 50°C higher than the maximum desorption temperature that will be used later in the experiment. The trap tube should be left for two to three hours at this elevated temperature. Cooling to ambient temperature should be done within a few minutes without any gas flow, to prevent new trapping of trace amounts of volatile from the gas stream.

For storage the manufacturers suggest that the tubes should be sealed using airtight end caps to prevent diffusion of VOCs from the ambient air onto the adsorbent material of the trap. However we have found that these end caps do not prevent the tubes adsorbing sufficient VOCs over a weekend to interfere with experiments. Therefore the strategy is to clean the tube, as described earlier, before using it after it has been stored for more than one day.

1.7 Defining Sensitivity and Detection Limit Calculations used for Thermal Desorption Experiments

Expressing the performance of the MS-200 the two expressions “Sensitivity” and “Detection Limit” are commonly used.

Using the standard double membrane pre-concentrator, the concentration inside the vacuum system is directly linked to the concentration of the sample gas on the outside of the membrane. Therefore the measurement results of the MS-200 can be directly related to a concentration in the sample gas stream. When using adsorbent traps, a specific volume of a sample is passed through the trap, and volatile compounds (dependent on the trap material) are trapped. This results in the amount of sample collected being dependent not only on the concentration in the sample stream, but also on the sampling volume.

One way to express the sensitivity using adsorbent tubes is to express it relative to the number of molecules, or the weight, of sample on the trap. This results in an expression of the sensitivity as counts per mole or counts per nano-gram of sample, rather than the counts per ppb as expressed when using the double membrane concentrator.

The sensitivity of the trap, S_{trap}, will be expressed as counts per mole or nano-gram, as shown in Equation 1:

$$S_{Trap} = \frac{Counts_S - Counts_B}{amount\_trapped}$$

$Counts_S$ = Counts in the target VOC peak in the Sample
$Counts_B$ = Counts in the target VOC peak in the Background

Equation 1: Sensitivity definition based on loading of adsorption tube

However, it is an advantage to be able to relate the sensitivity of the TED interface directly to the sensitivity of the double membrane inlet of the MS-200. To do this, the new sensitivity of the TED compared to the double membrane inlet, S_{AT}, will be expressed as counts per ppb per ml. This is shown in Equation 2:

$$S_{AT} = \frac{Counts_S - Counts_B}{Concentration * SampleVolume}$$

Concentration = Concentration of the Sample

Equation 2: Sensitivity definition based on concentration and sample volume

As in the sensitivity calculation for the double membrane inlet, the sensitivity calculation for the adsorption tubes is limited by the linear response of the analyser. In addition to the equations above, the break through volume of the adsorbent trap, described in section 1.4 has to be considered.

1.7.1 Theoretical Detection Limit for Adsorbent Tubes

The detection limit defines the point from which a signal, measured from a sample is not just a variation in the background measurement - i.e. noise. The US-EPA defines the detection limit, as the concentration at which the signal of the sample is three times the statistical variation σ in the background noise
The estimation of the detection limit for the double membrane inlet, assumes that the variation in background measurement, performed by the MS-200 is mainly due to the

variation caused by counting statistics. For the TED, the same relationship can be assumed - provided the adsorption tubes used to measure the background are cleaned to the same level. The theoretical detection limit, σ_{ThorAT} can then be calculated by the equation given below in Equation 3, where the detection limit is expressed in ppb*ml:

$$\sigma_{ThorAT} = \frac{\sqrt{Counts_B}}{S_{AT}}$$

σ_{Theor} = *Theoretical Detection Limit*

Equation 3: Theoretical detection limit for use of adsorbent tubes

1.8 Experimental Work

The procedure for analysis, when using the TED, is first to seal the tube onto the special inlet, as shown in Figure 1, followed by evacuating the desorption space to a pressure of approximately 1mbar. The evacuation pump is then switched off and the inlet to the MS-200 opened, in order to expose the desorption space to the inner membrane and allow permeation of the sample into the vacuum of the analyser chamber. In the next step, the adsorption tube is heated to perform desorption of the chemical of interest, before taking a spectrum in order to measure the instrument response to the chemicals on the adsorption trap.

1.8.1 Comparison of the TED with the standard membrane inlet

As an example of the increased sensitivity available with the TED a 20ppb sample of Benzene in a nitrogen matrix was used. After analysing a background, the adsorption trap was filled using 10ml sample of 20ppb benzene and analysed. Background measurement was 8,975 counts at 78amu (the main mass peak of benzene); the sample gave a 78amu signal of 18,507 counts.

Using Equation 2, this results in a sensitivity of $47^{counts}/_{(ppb*cc)}$. In order to be able to compare the results better with the double membrane inlet, the sensitivity was multiplied by the 10ml sampling volume, resulting in a sensitivity of 470counts/ppb. Comparing this to the sensitivity of the MS-200, using the double membrane inlet configuration, which was measured at $61^{counts}/_{ppb,}$ the TED improved the sensitivity by a factor of 7.7.

The theoretical detection limit, using Equation 3 in this case calculates to 2ppb*cc. Again dividing this by the sample volume, in order to ease comparison the theoretical detection

limit calculates to 200ppt. This means that the TED improves detection limit compared to the double membrane inlet (measured to 2.3ppb for 1σ) by a factor of 11.5 for benzene.

Another example of the comparison of detection sensitivity between the standard double membrane and the TED interface on a MS-200 is shown below on a selection of 7 alkanes: Using standards of each alkane in a nitrogen matrix the sensitivity of the standard double membrane inlet of the MS-200 was recorded. This consisted of first recording a nitrogen background, and then attaching a tedlar bag with the chemical of interest onto the inlet and drawing the sample across the outer membrane by means of the in-built sample pump.

Adsorbent traps, used for the TED study were filled with approximately 200 mg of Tenax TA. Between use the tubes where re-conditioned at 300°C for about 15 to 20 minutes with a flow of nitrogen of about 200 $^{ml}/_{min}$.

The gaseous samples in the tedlar bags were connected to the adsorption using a 30 mm long PTFE pipe and a 1/4" stainless steel union (from Swagelock). The amount of sample that was passed through the adsorbent trap was accurately metered using a 50 ml capacity soap film flow meter.
When loading the adsorbent trap, it is important to carefully evaluate the break through volume of the trap. Break through volumes for the tracers with the trap used are given in **Error! Reference source not found.**.

	Break through Volume for a 200 mg Tenax-TA trap [litre at 20°C]
Butane	0.160
Pentane	1
Heptane	20
Hexane, 2-methyl	20
Hexane, 3-methyl	20
Octane, 4-methyl	500
Decane, 5-methyl	2520

Analysis of the tubes were then performed in the following way using the TED interface, to see the impact of the improved sensitivity. First the freshly conditioned tube was connected to the TED interface of the MS-200. The tube then was evacuated using the peristaltic pump of the MS-200. Pumping is stopped when the pressure drops to less than 2 mbar and the evacuated region is sealed off. At this stage, the heater is switched on and the adsorption tube is heated to 250° C in order to desorb the analyte into the evacuated desorption space. Once the desorption temperature is reached (which takes about 60 seconds) the inlet valve to the mass analyser is opened, allowing the analytes in the intermediate vacuum space to permeate through the inner membrane of the inlet system into the vacuum of the mass analyser. Allowing two minutes for the sample to equilibrate, a ten second measurement of the analyte in the mass analyser was taken.

This recorded a background measurement for this specific tube. After cooling down, the tube was loaded with the analyte of interest and the analysis was repeated as in the background measurement, this time recording the response to a specific loading of the tube.

Figure 4: Detection Limit and Sensitivity Comparison between double membrane and TED for a selection of alkanes

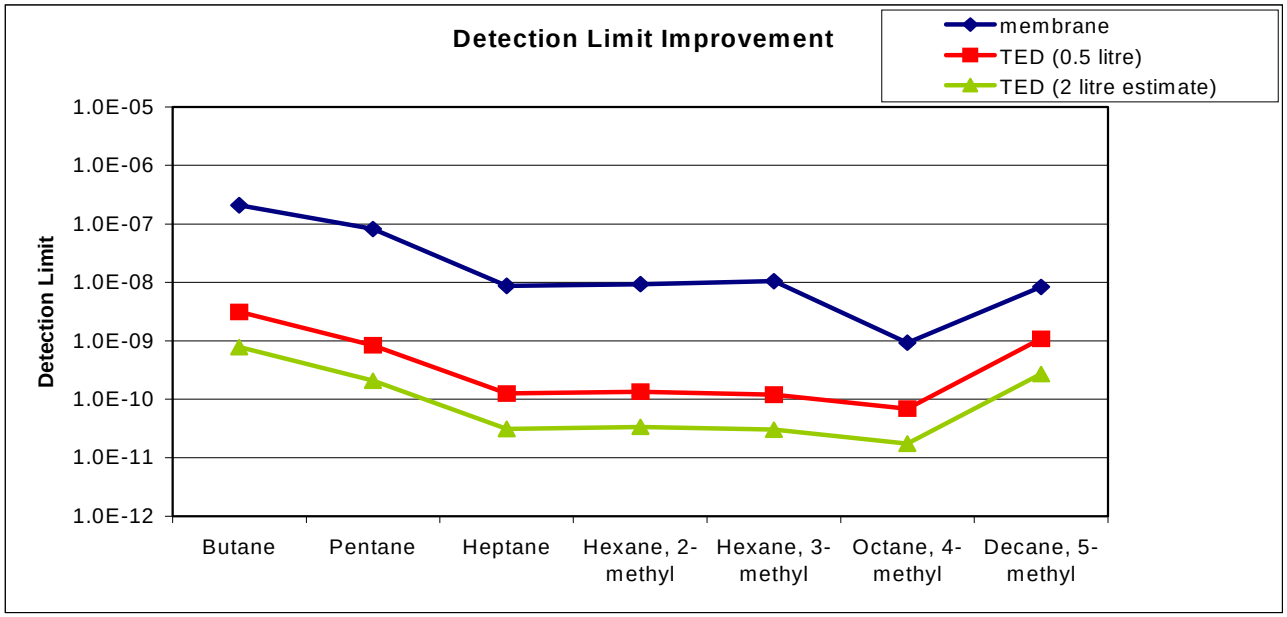

Fig 4 shows the result of the measurements for the alkanes, using the TED interface and the double membrane inlet. The dark blue line shows the detection limit for the alkanes using the standard membrane inlet of the MS-200. The dark red line shows the improvement that was achieved using the TED with a sampling volume of 0.5 litre. This sample volume was chosen in order to have sufficient loading of the alkanes on the trap and therefore produce a reasonable signal when measuring with the TED. From this signal the sensitivity is calculated for the alkanes. Choosing this sample volume, butane will have reached its break through volume, and therefore the values that are recorded are likely to be slightly higher if the break through volume were increased by cooling the trap during sampling.

The detection limit of the TED method is currently limited mainly by the variations in the counts of the background measurement and not by the sensitivity of the analyte. However, the background measurement in this method is independent of the sampling volume, and therefore chemical loading onto the trap. This allows an estimation of the

detection limit improvement for higher sampling volumes, using the assumption that the sensitivity is linear to the loading of the tube, which again is linear to the sample volume. This assumption is valid up to a point were an analyte reaches its break through volume on the trap, and sample loss occurs. For Fig.4 this means that the 2 litre estimated TED detection limits (green line) are over estimated for the two lightest alkanes as break through of the trap occurs after 0.16 litre for butane and 1 litre for pentane. For the remaining compounds the sample volume could be increased to 20 litres for Heptane, Hexane-2-methyl and hexane-3-methyl without loss of sample. The remaining alkanes have high break through volumes and therefore the detection limit for them could be improved significantly, simply by sampling for longer.

1.8.1 Using the TED with moist samples

Many applications require the measurement of VOCs in water or soil. Requiring the analyser to deal with water vapour.

Using benzene again as the test sample 1 litre of water was spiked with 10µl of benzene, producing a concentration of 10ppm of benzene in water. From this an aliquot of 5ml was taken to which another 495ml of water were added, producing 0.5l of 100ppb benzene in water. This 100ppb standard was filled into a 1-litre sample flask. After 30 minutes in order to allow for equilibration, 50ml of headspace above the water standard was sampled onto a cleaned adsorption tube. The tube was further conditioned, before analysis. The differential breakthrough volume of benzene and water was used to remove the water. The break through volume of the 31mg Tenax trap at 20°C for benzene is 2.17 litres and for water it is only 2ml. This differential meant that after sampling, the trap was purged using 20ml of dry nitrogen, which was sufficient to exceed the breakthrough volume for the water, and therefore purging the water from the trap, without exceeding the breakthrough for the benzene, which would result in a sample loss.

The background reported 13,967 counts for the major mass peak of benzene at 78amu. The measurement of the sample reported 443,904 counts. Above 300,000 counts, the peak is assumed to be saturated and linearity can no longer be assumed. However, it is still possible to estimate the sensitivity and detection limit, with the note that the actual sensitivity and detection limit will probably be better than the one calculated, based on the above results.

Therefore the sensitivity calculates to better than $43^{counts}/_{(ppb*cc)}$ for benzene in water. The detection limit of benzene in water is below 2.7ppb*cc. In this example with a sampling volume of 50ml the detection limit equals to 54ppt of benzene in water