PROCESS AND ENVIRONMENTAL APPLICATIONS OF GAS CHROMATOGRAPHY WITH THE REDUCTION GAS DETECTOR

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ABSTRACT
The Reduction Gas Detector (RGD) is routinely used for gas chromatographic analysis of volatile compounds that are readily oxidized. The RGD has a tiny amount of HgO in a heated assembly that reacts with volatile compounds as they pass over this bed of material. This causes traces of Hg to be released into a low volume flow cell with photometer for quantitative determination of the analyte. The traces of Hg are then scrubbed with activated charcoal. The HgO bed lasts for six months to two years and is easily changed. Impurities in nitrogen, oxygen, argon, helium, ambient air, carbon dioxide, and ammonia are readily analyzed by GC as the RGD does not react with these relatively stable gases. Hydrogen, carbon monoxide, arsine, phosphine, carbonyl sulfide are measured in ethylene and propylene for catalyst protection purposes. Ethylene, ethylene oxide, arsine, phosphine, nitric oxide, ketones, aldehydes, isoprene, 1,3-butadiene, and benzene are analyzed in ambient air for industrial hygiene and environmental reasons.

This paper discusses examples of GC/RGD analyses of ambient air and in chemical process monitoring applications of the Reduction Gas Detector for gas chromatography.

The difference between the RGD and the flame ionization detection (FID) of organic compounds is also discussed.

OPERATING PRINCIPLE OF THE RGD
The basic operating principle of the detector is based upon the strong absorption of UV light by mercury vapor. Compounds eluting from the column pass through a mercuric oxide bed that is heated. Reducing components, i.e. compounds that can combine with oxygen, react with the mercuric oxide and release mercury vapor. The free vapor evolved in the reaction is then detected by measuring the absorption of UV light in a photometric cell. The absorption is directly proportional to the concentration of the mercury vapor which is proportional to the concentration of the reducing analyte from the column.

The following general reaction takes place:

\[ X + \text{HgO (solid)} \rightarrow XO + \text{Hg (vapor)} \]

For H2 and CO the reactions are:

\[ \text{H}_2 + \text{HgO} \rightarrow \text{H}_2\text{O} + \text{Hg} \]
\[ \text{CO} + \text{HgO} \rightarrow \text{CO}_2 + \text{Hg} \]

This technique of sensing mercury vapor lends itself to part-per-trillion (ppt) and part-per-billion (ppb) detection limits of reducing compounds. Since the detector reacts only to reducing compounds, there is no interference from the matrix such as O2, Air, He, N2, Ar, CO2, etc. The actual detection limits are related to the reaction efficiency of different compounds in the mercury oxide bed as well as the sample volume injected into the column, the path length of the photometer cell, and the signal to noise level achieved through the system.
A cross sectional drawing of the detector is shown in Figure 1. The UV source is a mercury lamp with an optical filter and a reference photo diode detector to monitor lamp intensity fluctuations at 254 nm.

Figure 1. Reduction Gas Detector schematic.

The rest of the light travels via the light guide through the cell and out the other light guide through the 254 nm optical filter to the signal photo diode detector. The column effluent enters the HgO reaction bed which is heated to about 265°C, where the reducing compounds react and release mercury vapor. The light intensity will be different between the two photo diodes, depending upon the amount of mercury vapor in the cell. Signal processing electronics measure the difference between the two photodiodes, automatically canceling lamp flicker noise, and displaying the mercury vapor concentration. This is directly proportional to the concentration of a reducing compound eluting from the column system.

The low level of mercury vapor in the carrier gas flowing from the photo cell is trapped with a scrubber before entering the ambient atmosphere.

For the ultimate detection limit, it is important to have a carrier gas with a reliable negligible concentration of reducing species to optimize the detector signal to noise ratio.

ENVIRONMENTAL APPLICATIONS

H₂ and CO Analysis in the Atmosphere

The RGD is ideally suited for the determination of ppb to part-per-million (ppm) levels of H₂ and CO in atmospheric studies. CO is involved in ozone depletion, even at very low concentrations.

The RGD was mounted in an aircraft and was used by Dr. Paul Crutzen for his analyses of CO in the upper stratosphere. In these analyses, the Reduction Gas Detector is used to provide rapid and reproducible quantitative measurements.

This system was designed for trace levels of H₂ and CO in the atmosphere, where there is a possibility of other high molecular weight pollutants that could interfere with the determination.

Air carrier gas is preferred because it gives a minimum of upset in the baseline from the injection, is inexpensive, and readily available.

A 10-port valve is used to inject the sample from the sample loop to the stripper column. Lighter compounds, such as H₂ and CO, elute quickly from the stripper column into the analytical column, while higher molecular weight components such as hydrocarbons and moisture elute very slowly from the stripper column. After the light components have had sufficient time to elute from the stripper column into the analytical column, the 10-port valve returns to the load position. In addition to preparing the analyzer for the next sample injection, this valve position is used to backflush the higher molecular weight components from the stripper column to vent.

Backflushing of the stripper column accomplishes two objectives. It shortens the analysis time and it vents contaminants which can produce an unstable baseline away from the detector. Oxygen and nitrogen from the air will elute through the analytical column. However, these components do not interfere with the determination of H₂ and CO because of the chromatography and the selectivity of the RGD.

Ethylene Oxide in Ambient Air

The presence of ethylene oxide in ambient and indoor air should be monitored at less than the OSHA regulatory limit of one ppm to reduce the possibility of cancers in workers exposed to it.

A Reduction Gas Detector, with appropriate injection system and columns, responds to ethylene oxide at 20-30 ppb in ambient air (Table I and Figure 1).

In the RGD determination of ethylene oxide, a 10-port valve and a 1 mL sample loop is in the flow path of continuously flowing ambient air. The valve rotates to inject the sample to a stripper column, (inorganic phase). Light components, such as oxygen, are diverted from the stripper column to vent using a 4-port valve located downstream from the 10-port valve. After the oxygen elutes from the stripper column, this 4-port valve is programmed to return to its original position to transfer ethylene oxide to the analytical column (HayeSep). In this way, the 10-port valve and the 4-port valve divert the oxygen, carbon monoxide, and hydrogen to vent and away from the analytical column and RGD detector. The 10-port valve is programmed to return to its original position to transfer ethylene oxide to the analytical column (HayeSep). In this way, the 10-port valve and the 4-port valve divert the oxygen, carbon monoxide, and hydrogen to vent and away from the analytical column and RGD detector. The 10-port valve is programmed to return to its original sampling position once the ethylene oxide has been transferred to the analytical column, and at the same time, puts the stripper column in backflush mode to prevent the build up of moisture. The total cycle time between sequential injections in this work is 500 seconds (8.3 minutes).

Table I summarizes the results obtained generating different concentrations.
Table I  EtO in Air Analytical Data

<table>
<thead>
<tr>
<th>EtO (ppb)</th>
<th>Peak Area</th>
<th>Average</th>
<th>%SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2100</td>
<td>481,313</td>
<td>466,856</td>
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<td>2100</td>
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<td>2100</td>
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<tr>
<td>700</td>
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<td>150,658</td>
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<tr>
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<tr>
<td>700</td>
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<tr>
<td>50</td>
<td>10,856</td>
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</tr>
</tbody>
</table>

Figure 2 shows a typical spectrum with less than 1 ppm EtO.

PROCESS APPLICATIONS

H₂ and CO in Ethylene or Propylene

Making polyethylene or polypropylene from ethylene or propylene requires a catalyst, such as the Ziegler-Natta polymerization catalyst. The performance of this catalyst is adversely affected by CO, and it is of interest to determine this component at the ppb levels. In this analysis, the RGD is used to provide rapid and reproducible CO measurements.¹⁰

Unsaturated hydrocarbons give strong response in the RGD. When ethylene or propylene is a major component in the sample, it can overload the RGD as well as the analytical column, producing a long tailing peak that requires a long time to return to baseline. This application package is designed to overcome interference from the major unsaturated component by using special plumbing and column configuration.

Nitrogen carrier gas is used because it gives a minimum of upset in the baseline from the injection, is inexpensive, and readily available.

A 10-port valve is used to inject sample from the sample loop to the stripper column. Lighter compounds such as H₂ and CO, elute quickly from the stripper column into the analytical column while higher molecular weight components, such as hydrocarbons (principally ethylene and propylene) and moisture remain in the stripper column. After the light components have had sufficient time to elute from the stripper columns into the analytical column, the 10-port valve returns to the load position. In addition to preparing the analyzer for the next sample injection, the valve in this position is used to backflush the higher molecular weight components from the stripper columns to vent.

As mentioned previously, backflushing of the stripper column to vent shortens the analysis time and vents contaminants which can produce an unstable baseline.

Figure 3 shows a typical sample of propylene when the backflush is set after the ethylene peak; in the case of high ethylene concentrations, the backflush should be set before the ethylene peak to avoid excessive consumption of the mercury oxide bed.

The RGD is also sensitive to phosphine, arsine, and carbonyl sulfide, additional impurities that can adversely affect catalyst performances, as shown in Figure 4.
**H₂ and CO in Ammonia**

Ammonia purity used in the production of light emitting diodes or diode lasers is becoming more and more important to a successful manufacturing operation.

Setting the injection system in a way similar to the one mentioned previously, letting H₂ and CO pass over a stripper column and trapping NH₃, allows the analysis of H₂ and CO at trace level to be easily performed.

As shown in Figures 5 and 6, the calibration performed generating various concentrations in the 10-1000 ppb range provided good linear results and allowed detection in the range of 10 ppb.

Even better results, in terms of sensitivity, can be obtained for less reactive matrix gases such as Ar, N₂, H₂, O₂, and CO₂. Figure 7 shows a chromatogram of about 1 ppb H₂ and CO in a sample of ultra pure nitrogen.¹¹⁻¹³.

**CONCLUSIONS**

Some applications of a Reduction Gas Detector for gas chromatography have been briefly discussed.

Even if the RGD is not commonly used for the detection of organic compounds, it offers several advantages over the more traditional FID, such as a sensitivity about 50-100 times better and the lack of a requirement for service gases such as air or hydrogen.

The data presented in this paper were obtained with packed column; however, the low carrier gas flow rate required for its operation, 10 mL/minute, makes it suitable for use in combination with capillary columns, therefore allowing use for other applications.
REFERENCES


