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SELECTIVITY OF THE REDOX CHEMILUMINESCENCE DETECTOR FOR COMPLEX SAMPLE ANALYSIS

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SUMMARY

The redox chemiluminescence detector is a new selective detector for gas chromatography, based on catalyzed redox reactions of NO_2 or HNO_3 with reducing agents to form NO, which is subsequently detected by the ozone chemiluminescence technique. By change of some of the operating parameters of the redox chemiluminescence detector, including the active metal used as the catalyst and the temperature of the catalyst bed, the selectivity of the detector can be tailored to a particular analysis. When an elemental gold catalyst is used at a relatively low temperature (200–300°C), only those compounds that can be easily oxidized, such as alcohols, are detected, while at higher temperatures (>350°C), wider ranges of compounds produce a response, including aldehydes and ketones. When gold is used as the catalyst, alkanes are not detected except at quite high catalyst temperatures (>450°C). When palladium is used in the catalyst bed, even at lower temperatures (<300°C) more compounds produce a redox chemiluminescence detector response, including alkanes. Thus the selectivity of the redox chemiluminescence detector can be controlled to permit selective analysis for a wide range of sample types.

INTRODUCTION

Modern chromatographic systems possess tremendous resolving power; however, complex analyses are often complicated by an inability to separate all the components of a sample. Many analyses do not require identification of all the compounds present, and to this end the sample may be separated into fractions containing the compounds of interest and other fractions of lesser interest. Sample preparation and fractionation have the disadvantages of being time-consuming, sometimes introducing artifacts, contaminating the sample, and causing loss of analytes. Selective detection of only the compounds of interest in a complex sample eliminates the need to fractionate the sample, with these associated complications.

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A selective detector, capable of judiciously discriminating between classes of compounds, can enhance the detection capability of a chromatographic system by eliminating the response associated with other classes of compounds which are not of interest. When components of a sample are not completely resolved, quantitation can be improved if the selective nature of the detector causes it to be insensitive to the interfering compounds. This can be particularly valuable in the suppression of the response due to a large solvent peak or other components present at high concentrations.

The redox chemiluminescence detector is a post-column reaction detector which provides a wide range of selectivity for a variety of compound classes. The theory and operation of this detector have been recently described[1,2]. In the redox chemiluminescence detector, the effluent from a gas chromatographic column is mixed continuously with an excess of a reagent, such as nitrogen dioxide (NO_2), just prior to a heated catalytic reaction zone. In the catalyst bed, any compound that reduces NO_2 to nitric oxide (NO) produces a surrogate pulse of NO, which is subsequently detected upon reaction with ozone (O_3) further downstream to produce a chemiluminescence signal. The sensitivity and general characteristics with respect to the selectivity of the redox chemiluminescence detector have been discussed previously[2]. In order to be sensed by this detector, a compound must be able to reduce NO_2 (or another NO precursor) rapidly at a catalyst surface. The detector responds to hydrogen, carbon monoxide, carbon disulfide, hydrogen sulfide, sulfur dioxide, ammonia, hydrogen peroxide, formic acid, formaldehyde, phosgene, and other oxygen-, nitrogen-, and sulfur-containing compounds. The selectivity of the detector can be controlled by changing certain detector parameters such as: the operating temperature of the catalyst bed, the metal in the catalyst bed, the catalyst support material, and the reagent gas.

EXPERIMENTAL

Apparatus

The gas chromatographic redox chemiluminescence detector that we have constructed is described in an earlier publication[2]. It consists of the following parts: a purification train for the carrier gas supply, a chromatographic column, a reagent metering device, a redox reaction zone, an ozone source, a chemiluminescence measuring system, and a vacuum pump. The redox reaction region is a packed bed of borosilicate glass beads, which have been coated with a metal by precipitation and reduction to the elemental form, in a manner identical to that used in previous studies[1,2].

Redox reaction catalyst bed preparation

Preparation of the gold catalyst beads and fabrication of the catalyst bed are described in earlier work[2]. The palladium catalyst bed was similar, but consisted of a 4-mm I.D. Pyrex® glass tube, packed with 0.3 g of 0.1-mm diameter borosilicate glass beads, which had been coated with elemental palladium. The beads were prepared by evaporation to dryness of an aqueous solution of palladium chloride, followed by reduction under flowing hydrogen at 400°C. The metal loading on the glass beads was approximately 2% by weight.

Samples

A gasohol mixture was prepared by adding 5% by volume of methanol to a commercial, unleaded, regular gasoline sample (Sinclair Oil and Gas).

A simulated refinery gas sample was prepared by diluting a known volume of ethene and propene with a known volume of natural gas (Public Service Company of Colorado). The simulated refinery gas mixture contained approximately 90% (v/v) methane, 5% ethane, 3% air, 1% carbon dioxide, 1% propane, 0.09% ethene, and 0.05% propene.

An acid–neutral extract of a municipal wastewater sample was prepared by adjusting the pH of a 100-ml sample to a pH of 2 with dilute hydrochloric acid and extracting with three 30-ml portions of dichloromethane. The dichloromethane layer was dried over anhydrous sodium sulfate and concentrated using a Kuderna-Danish concentrator.

Volatile organic compounds in ambient air were collected in Boulder, CO, U.S.A. using a Tenax GC sorbent technique[3]. Two 10-l samples were collected using a vacuum pump (Metal Bellows, Sharon, MA, U.S.A.) and desorbed under flowing helium at 250°C into a cooled capillary column (–50°C). After desorption was complete (10 min), the column temperature was programmed from –50°C to 0°C at 20°C/min and then from 0°C to 250°C at 8°C/min.

Instrumentation

In the present study, three different chromatographic systems were used. The gasohol chromatograms were produced with an F & M 810 gas chromatograph (F & M Scientific, now a division of Hewlett-Packard, Avondale, PA, U.S.A.), modified with a Grob-type injector[4] for split injections with a capillary column. The column was a DB-1701 column, 25 m × 0.32 mm I.D. fused-silica with 0.25 μm of cross-linked polysiloxane (86% methyl and 14% cyanopropylphenyl) stationary phase (J & W Scientific, Rancho Cordova, CA, U.S.A.). Typical gas chromatographic conditions were 10 p.s.i. of helium head pressure (25 cm/s linear velocity) and a split ratio of 1:50. Helium was used as the chromatographic carrier gas, and was purified by passing it through a copper catalyst trap, followed by a 13X molecular sieve trap to remove oxygen and water. The detector was a Model 207 redox chemiluminescence detector (Sievers Research, Boulder, CO, U.S.A.), equipped with a gold catalyst bed.

The simulated refinery gas chromatograms were produced using a Hewlett-Packard 5750 gas chromatograph. The column was a 3 m × 1.2 mm I.D. stainless-steel tube, packed with Chromosorb 102, 60–80 mesh (Manville Corporation, Denver, CO, U.S.A.). Helium was the carrier gas at a flow-rate of 30 ml/min. The detector was a Model 10 NO/NO_x chemiluminescence analyzer (Thermo Electron Corporation, Waltham, MA, U.S.A.) which was modified extensively in a manner similar to that previously described[2]. The redox chemiluminescence detector was serially coupled to the exit of a Hewlett-Packard thermal conductivity detector. This allowed simultaneous acquisition of the redox chemiluminescence detection (RCD) and thermal conductivity detection (TCD) chromatograms during the same sample analysis.

The chromatograms of the wastewater extract and the volatile organic compounds sorbed from ambient air were produced using a Hewlett-Packard 5890 gas chromatograph. The column was a Hewlett-Packard 25 m × 0.32 mm I.D. Ultra No. 1 with 0.52 μm of cross-linked dimethyl polysiloxane stationary phase. The detector was a Model 207 redox chemiluminescence detector (Sievers Research), equipped with a gold catalyst bed.

RESULTS AND DISCUSSION

The redox chemiluminescence detector can selectively detect reducing compounds of interest in the presence of non-reactive matrix components. Water, dichloromethane, and the major constituents of air (nitrogen, oxygen, carbon dioxide, and argon) do not produce a RCD response at the most frequently used operating temperatures (250–400°C) when gold is used as the catalyst. The RCD response to some compounds increases as a function of catalyst temperature; therefore, some compounds which are not responsive at normal operating temperatures reduce NO_2 to NO if a higher catalyst temperature is utilized. Through use of different catalyst bed temperatures the selectivity of the redox chemiluminescence detector can be varied to suit the analysis.

Fig. 1 presents the results of the gasohol analysis performed at different gold catalyst bed temperatures. At a gold catalyst temperature of 360°C the redox chemiluminescence detector responds only to methanol. When the catalyst temperature is raised to 390°C, the selectivity is lessened to permit detection of other components of the gasoline, such as the aromatic fraction, but not the saturated alkanes. When

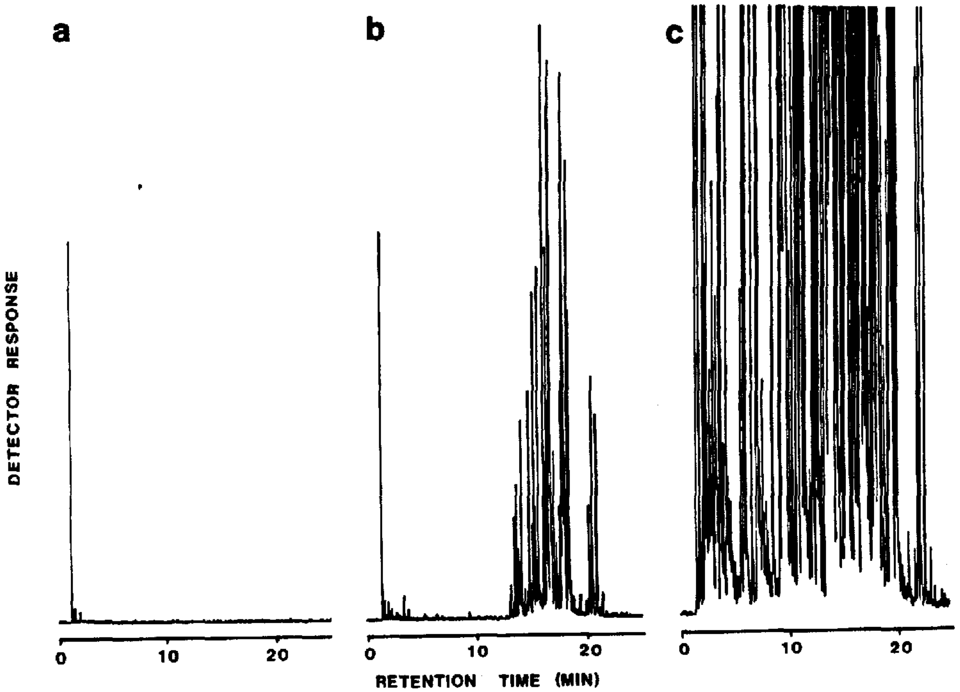

Fig. 1. Redox chemiluminescence chromatogram of a gasohol analysis, performed at different gold catalyst bed temperatures. (a) At 360°C only methanol is detected; (b) at 390°C methanol and the later eluted aromatic fraction components of gasoline are detected; (c) at 420° the analysis is even less selective, producing a chromatogram as complex as that of a flame-ionization detector. Gas chromatographic (GC) conditions: 1 min at 30°C, programmed to 250°C at 6°C/min, 1.4 μl split injection.

the temperature of the catalyst is raised to 420°C a chromatogram as complex as that from a flame-ionization detector is obtained. Due to the temperature-dependent response of the redox chemiluminescence detector, careful control of the catalyst bed temperature ($\leqslant \pm 2$°C) is essential to ensure reproducible results. A relative standard deviation of 1.2% for detection of carbon monoxide in gaseous mixtures has been achieved for repetitive loop injections at constant temperature (400 ± 2°C).

The observation[1] that gold catalyzes certain oxidation–reduction reactions involving NO_2 prompted the investigation of other metals for use as catalysts. Copper, silver, and rhodium show some catalytic activity, and palladium is particularly active in that it catalyzes the reduction of NO_2 to NO by alkanes. When gold is used in the catalyst bed, alkanes are not detected by the redox chemiluminescence detector, except at quite high catalyst temperatures (>450°C). Alkanes produce a response when palladium is used as the metal in the catalyst bed at operating temperatures as low as 250°C. Perhaps this response is a consequence of the greater dehydrogenation activity of palladium compared to that of gold[5]. Because hydrogen produces a response in both gold- and palladium-catalyzed RCD systems, secondary reactions may become important in the redox chemiluminescence detector at high temperatures, at which dehydrogenation may occur in addition to catalyzed reactions of NO_2.

Fig. 2 demonstrates the change in selectivity that can be achieved by using different metal catalysts. Fig. 2 shows the chromatograms of a simulated refinery gas sample detected with a thermal conductivity detector, the redox chemiluminescence detector containing palladium catalyst, and the redox chemiluminescence detector containing gold catalyst. The RCD chromatograms exhibit broader peaks, in part due to the increased dead-volume, resulting from serially coupling the redox chemiluminescence detector to the exit of the thermal conductivity detector. When palladium catalysts are used, there is some intrinsic peak broadening, in contrast to the sharp peaks observed with gold catalysts.

The RCD chromatogram with palladium shows response to both saturated and unsaturated hydrocarbons. When palladium is used, the molar response of the unsaturated hydrocarbons is much greater than that of the saturated hydrocarbons. This is important for samples in which the saturated hydrocarbons are present at much higher concentrations than the unsaturated hydrocarbons. The TCD chromatogram illustrates that, although the alkanes give observable peaks, the alkenes are barely seen above the baseline. Consequently, the selectivity of RCD offers attractive advantages for the analysis of samples containing small concentrations of unsaturated compounds in much higher concentrationjs of paraffinic compounds. It should also be noted that air produces a large, simultaneously eluted peak in the TCD chromatogram, while no interfering air peak appears in either of the RCD chromatograms.

Fig. 2 also compares the use of gold and palladium in the redox chemiluminescence detector and illustrates the effect on selectivity of changing the catalyst metal. In the chromatogram of the simulated refinery gas, only the alkenes give a response when gold is used, and there is no detectable response or interference from the alkanes. If the alkenes were of interest in an analysis, then this increase in selectivity by using gold instead of palladium would give the desired effect of eliminating interferences from alkanes eluted with little or no separation.

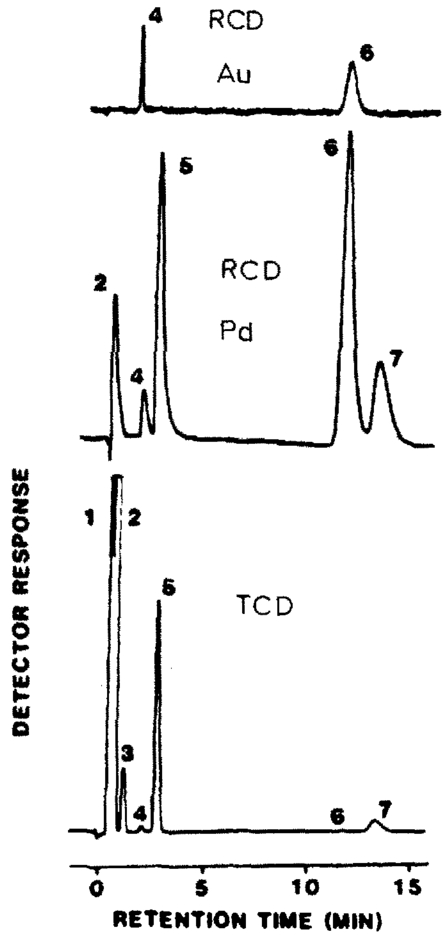

Fig. 2. Redox chemiluminescence detector analysis of 0.5 ml of a simulated refinery gas sample, performed using different metal catalysts. The bottom chromatogram shows a thermal conductivity detector response for the mixture: 1 = air; 2 = methane; 3 = carbon dioxide; 4 = ethene; 5 = ethane; 6 = propene; and 7 = propane. The upper chromatogram shows that with gold as the catalyst for the redox chemiluminescence detector only ethene and propene are detected. The middle chromatogram shows that with palladium as the catalyst for the redox chemiluminescence detector, methane, ethane, ethene, propane, and propene are detected. GC conditions: 50°C (isothermal), 0.5 ml injection. Detector conditions: thermal conductivity detector bridge current, 200 mA; redox chemiluminescence detector catalyst temperature, 300°C (gold), 400°C (palladium).

Fig. 3 shows the results from the analysis of the acid/neutral extract of municipal wastewater when a flame-ionization detector and the redox chemiluminescence detector are used. Unlike the flame-ionization detector, the redox chemiluminescence detector does not respond to dichloromethane. Therefore, certain volatile species which are normally obscured by the solvent peak, can be detected by the redox chemiluminescence detector. The selectivity of the redox chemiluminescence detector results in a less complex chromatogram than obtained with the flame-ionization detector. Because the redox chemiluminescence detector (with gold as a ca-

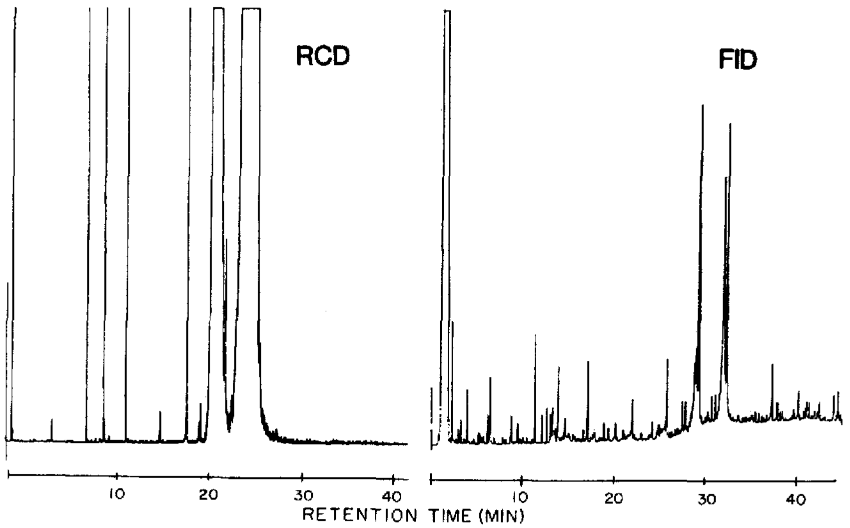

Fig. 3. Analysis of a dichloroimethane acid–neutral extract of municipal wastewater with a flame-ionization detector and a redox chemiluminescence detector. GC conditions: 1 min at 20°C, programmed to 300°C at 8°C/min, 2 μl splitless injection. Detector conditions: flame-ionization detector, attenuation, × 4; range, 4; redox chemiluminescence detector catalyst temperature, 300°C; integration time, 0.5 s.

talyst) does not respond to saturated hydrocarbons, which are usually present in municipal wastewaters, direct analysis of oxygenated compounds such as phenols and phthalate esters is possible.

The results from the analysis of volatile organic compounds in ambient air, obtained with the flame-ionization detector and the redox chemiluminescence detector are shown in Fig. 4. While the flame-ionization detector responds to virtually all of the organic compounds in ambient air, the selectivity of the redox chemiluminescence detector yields a much simpler chromatogram. Specifically, the redox chemiluminescence detector does not respond to the saturated hydrocarbons, which are usually present at high concentrations and mask the presence of trace oxygenated species, including aldehydes, ketones, and carboxylic acids. The RCD chromatogram shown in Fig. 4 was obtained at a gold catalyst temperature of 200°C. At this temperature, oxygenated compounds produce a response, while aliphatic, olefinic, and aromatic hydrocarbons do not. By operating the redox chemiluminescence detector catalyst at a higher temperature, analysis of the olefins, aromatic hydrocarbons, and trace oxygen-containing species in ambient air should be possible, without interference from aliphatic hydrocarbons.

The chemical reactivity of supported noble metals in other reactions has been shown to vary significantly as a function of composition of the support material[6–9]. Thus, changing the catalyst support from borosilicate glass or silica to alumina or magnesia may provide an additional parameter for tailoring the selectivity of the redox chemiluminescence detector for specific analyses.

In the normal operation of the redox chemiluminescence detector, dilute NO_2 is constantly admitted to the catalyst chamber. In the heated catalyst bed, a small amount of thermal decomposition of NO_2, which produces NO, generates a low

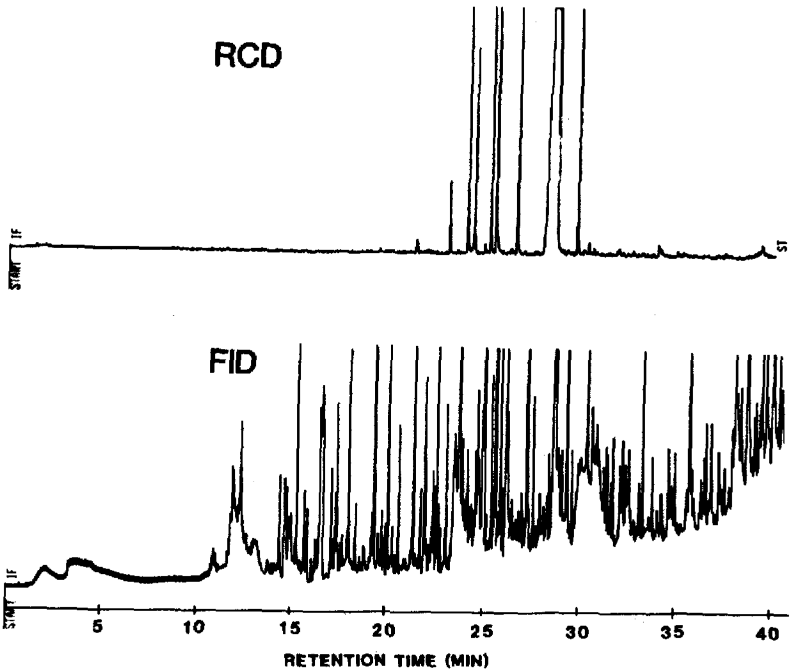

Fig. 4. Volatile organic compounds in ambient air of Boulder, CO U.S.A. Two 10-l samples, sorbed on Tenax GC, desorbed at 250°C, and analyzed using FID and RCD. GC conditions: 10 min at −50°C programmed to 0°C at 20°C/min, then programmed to 250°C at 8°C/min. Detector conditiosns: flame-ionization detector, attenuation, × 4; range, 3; redox chemiluminescence detector catalyst temperature, 200°C; integration time, 0.5 s.

background signal. Recent work has confirmed that a hot, supported metal catalyst adsorbs nitrogen-containing oxidants and retains them for a finite period of time. After passing gaseous NO_2 or HNO_3 (diluted in helium) through a gold catalyst bed for a short period, the flow was stopped so that pure helium flushed the catalyst bed. Subsequent injection of samples of methanol liberated NO, indicating that nitrogen in some form is sorbed on the gold surface. This phenomenon can potentially improve the limits of detection for trace level analysis, since the catalyst can be exposed to NO_2 reagent gas during a "loading" or equilibration period, and then, just prior to performing an analysis, the NO_2 flow can be discontinued to reduce the production of background NO. In this way, the signal-to-noise ratio should be improved, providing greater effective sensitivity and a lower minimum detectable limit for compounds of interest.

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