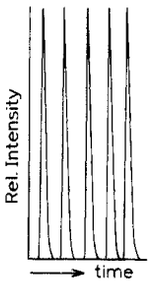

Figure 7. Repetitive injection of 10^{-5} M of H_2O_2.

after the TCPO has been deleted. One packing can continuously be used for about 8 h.

To test the reproducibility of the system, H_2O_2 solutions were repeatedly injected. The relative standard deviation for 10^{-5} M H_2O_2 was 0.9% (Figure 7) and 2.5% for 10^{-7} M. Detection limits were about 1×10^{-8} M H_2O_2 (0.3 ppb). Calibration curves were linear up to 10^{-4} M.

CONCLUSION

The use of immobilized fluorophores in conjunction with a solid-sate TCPO reactor permits a considerable simplification of the peroxy oxalate chemiluminescence system for H_2O_2 detection. Thus no additional pumps for reagent delivery are needed and mixing problems are also eliminated. The use of glass beads as support material has advantages over other supports such as silica gel or cellulose. A marked reduction of band broadening and a higher sensitivity are obtained by ths approach and, in addition, the choice of suitable fluorophores is widened since parameters such as solubility, costs, and toxicity do not play as much of a role.

Optimization with regard to the instrumentation and working conditions for an application to field analysis of rain water is in progress. The combination of this detection principle with dynamic systems generating H_2O_2 such as enzymatic and photochemical reactions in HPLC, bio- and immunoassays, etc. is also under investigation.

Registry No. TCPO, 1165-91-9; H_2O_2, 7722-84-1; H_2O, 7732-18-5.

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Redox Chemiluminescence Detector: Application to Gas Chromatography

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A new chromatographic detector is based on redox reactions coupled with measurement of chemiluminescence. Measurements involve the catalyzed postcolumn reduction of nitrogen dioxide by analytes that can readily be dehydrogenated or oxidized, followed by subsequent downstream oxidation of the formed nitric oxide by reaction with ozone. The redox chemiluminescence detector (RCD) responds to compounds that are not sensitively detected by flame ionization detectors (FID) such as ammonia, hydrogen sulfide, carbon disulfide, sulfur dioxide, hydrogen peroxide, hydrogen, carbon monoxide, formaldehyde, and formic acid. The RCD is also sensitive to alcohols, aldehydes, ketones, acids, amines, olefins, aromatic compounds, sulfides, and thiols. Sensitivity of the RCD is comparable with that of the FID. The RCD is not sensitive to the major constituents in the matrices of many samples, such as alkanes, chlorinated hydrocarbons, water, nitrogen, oxygen, and carbon dioxide. Relative molar response factors range over 6 orders of magnitude.

Advances in chromatographic analysis often evolve from increased sensitivity that allows detection of lesser amounts of materials, or from selective detection of only certain components of interest in a complex mixture of many compounds. The goal is often to detect and quantify certain components such as, nitrogen-, oxygen-, or sulfur-containing species, in the presence of much higher concentrations of less significant compounds that constitute the matrix, such as alkanes, water, or the major constituents of air.

Several recent, successful approaches to selective detection involve detection of postcolumn reaction products, especially for liquid chromatographic applications (*1-4*). After chromatographic separation, a reactant is mixed with the column effluent and a reaction occurs which produces a more readily detectable compound—either a derivatized analyte or other reaction product.

Chemiluminescence has been used to achieve very sensitive detection of compounds that react to form light-emitting

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species (*5*, *6*). Chemiluminescence detectors which are selective for polyhalogenated hydrocarbons (*7*), certain metal ions (*8*), and, of course, the flame photometric detector (FPD) for sulfur (*9*) have also been described. An olefin-selective detector has been based on the chemiluminescence accompanying the reaction of ozone with unsaturated compounds (*10*). Gas chromatography detectors that use homogeneous gas phase chemiluminescence reactions have been described which afford selective detection of ammonia and amines (*11*), N-nitroso compounds (*12*, *13*), and nitrogen-containing compounds (*14*, *15*).

The previous detectors (*11–15*) for nitrogen-containing compounds are all similar in operation in that the nitrogen contained in the analyte is converted to nitric oxide (NO), which is subsequently mixed with an excess of ozone (O_3) in a reaction chamber at reduced pressure, to produce electronically excited nitrogen dioxide (NO_2*) by the following reaction:

$$NO + O_3 \rightarrow NO_2^* + O_2 \quad (1)$$

The excited NO_2* relaxes to the ground state by photoemission in the visible and near-infrared region of the spectrum. The intensity of the emission is proportional to the concentration of NO and can be detected by a photomultiplier tube (*16*)

$$NO_2^* \rightarrow NO_2 + h\nu \quad (2)$$

With careful choice of photomultiplier tube response characteristics, optical filter, reaction chamber size, pumping capacity, reaction chamber pressure, and O_3 concentration, the NO/O_3 measurement technique has proven to be highly sensitive, rapid, linear over several orders of magnitude, and free from interferences (*17–20*). Many commercial instruments are available, and even more sensitive instruments have been perfected recently (*21–23*). The research instruments are capable of nearly continuous measurement of <0.01 ppb of NO, with very high specificity (*6*, *23*).

We have developed a new instrument called a redox chemiluminescence detector (RCD) which is both selective and sensitive. The RCD combines new catalyzed postcolumn redox reactions with sensitive chemiluminescence detection of NO. Nitrogen dioxide (NO_2) is mixed with the analyte continuously in a postcolumn gold catalyst bed, and NO is formed when the analyte present can rapidly reduce the NO_2. The RCD responds to compounds that serve as reducing agents, such as alcohols, aldehydes, olefins, and carboxylic acids, and it is insensitive to most compounds which constitute the bulk matrix of many environmentally and industrially important samples. The unique capabilities of the RCD allow detection of trace components of complex mixtures without time-consuming and potentially complicating sample preparation, work-up, or fractionation and provides a wide range of applicability as an analytical instrument.

EXPERIMENTAL SECTION

Apparatus. The gas chromatographic redox chemiluminescence detector (RCD) we have constructed is shown schematically in Figure 1. It consists of the following parts: a purification train for the carrier gas supply, a chromatographic column, a reagent metering device, a redox reaction catalyst zone, an ozone source, a chemiluminescence measuring system, and a vacuum pump. The diluent gas which carried the NO_2 into the catalyst zone was passed through a series of traps to remove trace-level reducing impurities. R3-11 copper catalyst removed oxygen, Hopcalite removed carbon monoxide, and 13X and 5A molecular sieves removed water and carbon dioxide. Sensitivity of the detector is strongly dependent on gas purity. This helium was then metered at 30 mL/min over a Kin-Tek Laboratories FEP Teflon NO_2 permeation device thermostated at 25 °C. The permeation tube loss rate of NO_2 was gravimetrically determined to be 11 μg/min. This NO_2 reagent in helium entered a Pyrex glass tee, coaxially sweeping the effluent of a gas chromatographic column directly into the

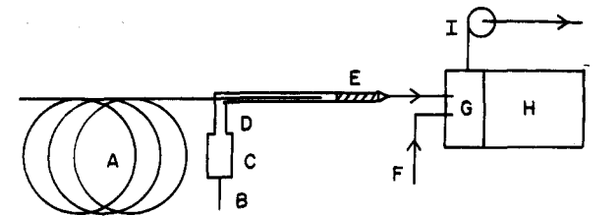


Figure 1. Schematic of the redox chemiluminescence detector (RCD) used with a gas chromatograph: A, capillary GC column; B, inlet for purified helium carrier; C, NO_2 permeation device; D, inlet for NO_2/helium reagent gas; E, heated catalyst zone for redox reaction; F, inlet for O_3; G, chemiluminescence reaction chamber; H, photomultiplier tube and electronics; I, vacuum pump.

redox reaction region. The reaction zone and the dopant addition tee were fabricated from the same piece of 2 mm i.d. Pyrex glass tubing. The redox reaction region consisted of a bed of 230–325 mesh borosilicate glass spheres which had been coated with precipitated, elemental gold in a manner similar to that used to support gold in other studies (*24*, *25*). This redox reaction region was heated externally to a typical operating temperature of 150 °C to 400 °C with several turns of Nichrome wire. The exit of the reaction region is connected to a modified commercial NO/NO_x chemiluminescence detector which operates based on the well-known reaction of NO with O_3 (*16*), as shown in eq 1 and 2. Flow was maintained through the redox reaction region and the chemiluminescence reaction chamber by the vacuum pump associated with the NO/NO_x instrument. Most of the residual NO_2 and O_3 was removed by a charcoal bed downstream from the vacuum pump, and the effluent was discharged to a fume hood.

Redox Reaction Catalyst Bed Preparation. One gram of 230–325 mesh glass beads was added to an aqueous solution of 0.5 g of $HAuCl_4 \cdot 3H_2O$. The solution was evaporated to dryness, then the beads were dried further at 110 °C for 2 h at 0.5 torr. The yellowish gold salt covered beads were then heated at 400 °C for 2 h under flowing hydrogen to form a metallic layer of elemental gold on the surface of the glass beads. Then the beads were rinsed with water, dried in air, and treated under flowing hydrogen at 400 °C for an additional 6 h. The gold-coated spheres (ca. 0.015 g) were packed loosely into a 1 cm length of the Pyrex glass reaction zone using silanized glass wool plugs at both ends to immobilize the bed.

Reagents. Hopcalite was supplied by Mine Safety Appliances Company, Pittsburgh, PA. The R3-11 copper catalyst was obtained from Chemical Dynamics Corp., South Plainfield, NJ. The NO_2 used to fill the permeation tube was Research Purity grade supplied by Matheson and was purged with oxygen, while in an ice bath, to remove any impurity NO. Reagent grade gold chloride was used as received from Fisher Scientific Co. The 230–325 mesh borosilicate glass beads were from F & M Scientific Corp., Avondale, PA (now a division of Hewlett-Packard). Before being coated with gold, they were washed in an ultrasonic bath using methanol and then water as solvents and dried in air.

Instrumentation. An F&M 810 gas chromatograph was modified with a Grob-type injector (*26*) for split injections with a capillary column. Typically, a J&W Scientific 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 was used. Typical gas chromatographic conditions were 10 psi 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. A stainless steel tee was used as a simple detector splitter to direct the chromatographic column effluent to both a flame ionization detector (FID) and the RCD when simultaneous detection was desired. A Model 14D NO/NO_x detector, obtained from Thermo Electron Corp., Waltham, MA, was modified by eliminating all internal plumbing with the exception of the ozone generator and the single NO monitoring reaction chamber. The ozone generator was supplied with pure industrial grade oxygen, the NO sample inlet was supplied directly from the heated redox reaction zone. To obtain the chromatogram of lemon oil, a Model 207 redox chemiluminescence detector, supplied by Sievers Re-

search, Inc., Boulder, CO, was substituted for the Thermo Electron detector. The column was a Hewlett-Packard Ultra-Performance No. 1 cross-linked methyl silicone capillary column, 25 m × 0.32 mm i.d.

RESULTS AND DISCUSSION

Theory of Operation. In the newly developed redox chemiluminescence detector, the effluent from a gas chromatographic column is dynamically mixed with a metered flow of dilute NO_2 and passed through a catalyst chamber. Responsive compounds react in this region to reduce NO_2 to NO, producing a surrogate pulse of NO for each reducing compound, which is then measured downstream by subsequent reaction with O_3 to produce a chemiluminescence response. The general reaction by which nitric oxide is produced is

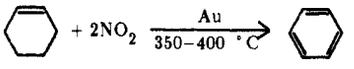
$$\text{reducing agent} + NO_2 \xrightarrow[150\text{–}400\ ^\circ C]{Au} \text{oxidized species} + NO \quad (3)$$

Specific examples, in which products have been identified, follow:

$$CH_3CH_2CH_2CH_2CH_2OH + NO_2 \xrightarrow[150\text{–}200\ ^\circ C]{Au} CH_3CH_2CH_2CH_2CHO + NO + H_2O \quad (4)$$

$$CH_3C(OH)HCH_2C(CH_3)HCH_3 + NO_2 \xrightarrow[150\text{–}200\ ^\circ C]{Au} CH_3C(=O)CH_2C(CH_3)HCH_3 + NO + H_2O \quad (5)$$

$$CH_3C(=O)CH_2C(CH_3)HCH_3 + NO_2 \xrightarrow[350\text{–}400\ ^\circ C]{Au} CH_3C(=O)CH=C(CH_3)CH_3 + NO + H_2O \quad (6)$$



(7)

From the illustrations, one can conclude that primary alcohols are oxidized to aldehydes, secondary alcohols to ketones, ketones to α,β-unsaturated ketones, and cyclic olefins to aromatic compounds. These reactions can all be viewed as catalyzed dehydrogenations. It is clear that other catalyzed redox reactions also produce nitric oxide by oxidation not involving dehydrogenation. Examples are the oxidation by nitrogen dioxide of carbon monoxide, sulfur dioxide, and carbon disulfide, none of which contain hydrogen.

For a chromatography detector to produce sharp peaks, any postcolumn reactions must occur very rapidly in a rather small reaction zone. Without a catalyst, most reactions of separated analytes with NO_2 do not occur rapidly enough to be useful for chromatographic detection. However, gold and a few other metals can catalyze reactions of NO_2 with compounds that can readily be oxidized at elevated temperatures to rapidly produce the NO which is subsequently detected. Extensive studies of a variety of catalyst bed configurations and compositions have led us to select a gold catalyst bed only 1 cm in length and 2 mm in diameter, which is typically maintained at temperatures from 150 °C to 400 °C. The combined flow rates of the column and the helium carrying the NO_2 to the catalyst bed were varied from 10 to 150 mL/min, with 30 mL/min chosen as optimum for the particular configuration used for most of the tests.

The activity of the gold catalyst is particularly striking when one considers that the calculated residence time in the 1 cm long catalyst chamber is only a few milliseconds. The actual time may be longer if adsorption of the analyte occurs, but the reaction that forms NO must occur within about a second, or otherwise the capillary chromatography peaks arising from detection of NO downstream would be broadened appreciably. The NO_2 is continuously fed into the redox reaction zone at concentrations from 5 to 500 ppm (typically ~100 ppm). The effective dead volume of the redox catalyst zone is smaller than it appears because the vacuum pump maintains the chamber well below atmospheric pressure. Accordingly, peak broadening is kept to a minimum and the detector can be used with capillary columns.

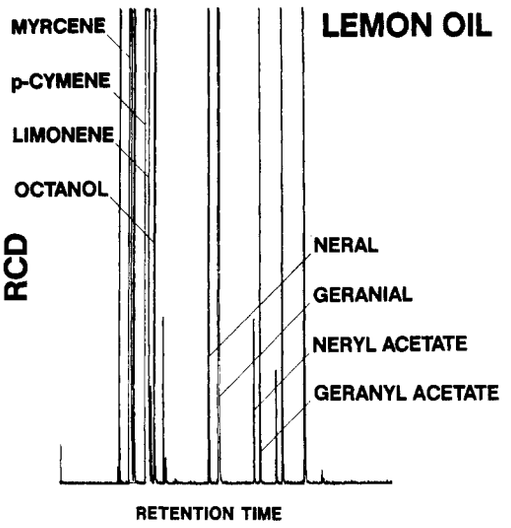


Figure 2. Chromatogram showing the response from the Model 207 redox chemiluminescence detector for the analysis of lemon oil. Each peak arises from a pulse of NO generated by the catalyzed reduction of NO_2 by the compound shown. Column temperature was 40 °C for 1 min, programmed to 60 °C at 20 °C/min, then to 250 °C at 4 °C/min.

Selectivity of the Redox Chemiluminescence Detector. Low molecular weight paraffins appear to be quite inert to gold-catalyzed oxidation at 400 °C, as indicated by the absence of any detectable NO at retention times corresponding to alkanes. Species that cannot be oxidized, such as water, carbon dioxide, argon, and oxygen, do not produce responses; furthermore, common compounds such as methylene chloride, 1,2-dichloroethane, tetrachloroethylene, and tetrahydrofuran do not generate appreciable responses under the conditions tested with the gold catalyst (400 °C). Consequently, the RCD often produces a less complicated chromatogram than the FID and, like a nitrogen–phosphorus detector (NPD), gives an indication of the possible classes of compounds present. In contrast with the NPD, however, the RCD response depends on the ability of a compound to serve as a reducing agent rather than on the presence of a specific element. Similarly, the RCD differs from the nitrogen-specific chemiluminescence detectors reported earlier (*14*, *15*). Compound classes which are detected by the RCD include alcohols, aldehydes, ketones, acids, phenols, olefins, aromatic hydrocarbons, amines, thiols, sulfides, and phosphonates. Figure 2 shows the detection of myrcene, *p*-cymene, limonene, octanol, neral, geranial, neryl acetate, and geranyl acetate by RCD.

Compounds were screened initially to determine whether or not they produced a response by injection of either dilute solutions or headspace gases into a capillary chromatographic column, with simultaneous FID and RCD detection. Table I lists compounds which produced a RCD response. It should be noted that the RCD responds particularly well to oxygen-, nitrogen-, and sulfur-containing compounds, because they can be readily dehydrogenated or oxidized by NO_2. Especially significant is the ability of the RCD to respond to a large number of sulfur-containing compounds, ranging from hydrogen sulfide, carbon disulfide, and organic sulfides to sulfur dioxide. While selective detectors are available for sulfur-containing or nitrogen-containing compounds, no practical detectors selective for oxygen-containing compounds in alkane matrices have been accessible until now.

Further insight into the chemistry upon which the RCD is based was obtained from experiments in which individual pure compounds that were known to produce a NO/O_3

Table I. Compounds That Produce a RCD Response

C_1 to C_{10} 1-alcohols	1-nitropropane
2-pentanol	2-nitropropane
2-octanol	*tert*-butyl disulfide
4-methyl-2-pentanol	1-octanethiol
benzyl alcohol	tetrahydrothiophene
2-phenylethanol	benzene
3-phenylpropanol	toluene
C_1 to C_{10} *n*-aldehydes	naphthalene
benzaldehyde	1-methylnaphthalene
p-tolualdehyde	indole
anisaldehyde	tetrahydrofurfuryl alcohol
phenylacetaldehyde	ammonia
C_1 to C_4 *n*-carboxylic acids	carbon disulfide
acetone	hydrogen peroxide
butanone	hydrogen
4-methyl-2-pentanone	carbon monoxide
5-nonanone	sulfur dioxide
aniline	hydrogen sulfide
2,6-dimethylaniline	diethyl ethylphosphonate
N,N-dimethylaniline	triethyl phosphite
2,6-dimethylphenol	tri-*n*-butyl phosphite
cyclohexene	dibutyl phosphite
2-hexene	triethyl phosphate
1-methylcyclohexene	

chemiluminescence signal after reaction with NO_2 at gold surfaces were injected into the gas chromatograph. Analysis of the reaction products showed that NO_2 is reduced to NO and that the injected compound is oxidized to a corresponding product (*27*). For example, in experiments involving sorbent collection of products followed by gas chromatography/mass spectrometry (GC/MS), 1-pentanol was oxidized to pentanal, and 4-methyl-2-pentanol was oxidized to 4-methyl-2-pentanone. In addition to nitric oxide, water was also a product of these reactions. The gold catalyst clearly promotes the coupled reduction of NO_2 to NO with the concomitant organic oxidation, since with uncoated glass beads under identical conditions neither NO nor appreciable quantities of the oxidized product were observed.

Response of RCD to Analytes Not Detectable by FID. The RCD is complementary to the FID, because many compounds that do not produce a FID response can act as reducing agents and be detected sensitively. For example, the flame ionization detector does not respond sensitively to formaldehyde, formic acid, carbon monoxide, hydrogen, ammonia, hydrogen peroxide, hydrogen sulfide, carbon disulfide, and sulfur dioxide, while the redox detector senses all of these. Figure 3 presents chromatograms which were produced by splitting the effluent of the GC to the FID and RCD after separation. The sample was an aqueous solution of formic acid, hydrogen peroxide, and butanoic acid. Butanoic acid can be sensed by both detectors, but only the RCD detects formic acid and hydrogen peroxide. It is worth noting that although hydrogen peroxide is best known as an oxidizing agent, it can also function as a reducing agent, as it does here. Because hydrogen peroxide is unstable, independent GC/MS experiments were conducted to ensure that the peak was arising from the elution of intact H_2O_2. A 1% aqueous solution of H_2O_2 produced a total ion chromatogram with a large "overloaded" water peak followed by a small sharp peak, the mass spectrum of which contained a m/z signal at 34, consistent with what would be expected for ionization of H_2O_2. The absence of a response by the RCD to $\sim$1 μL of water is particularly interesting because NO_2 is known to react with water to form NO and nitric acid. Apparently the contact time with the gold catalyst is too short for appreciable reaction to occur, while it is quite sufficient for reducing agents such as formic acid, hydrogen peroxide, and butanoic acid to form NO. The data in Table I demonstrate the value of the RCD for detecting several compounds to which currently used GC

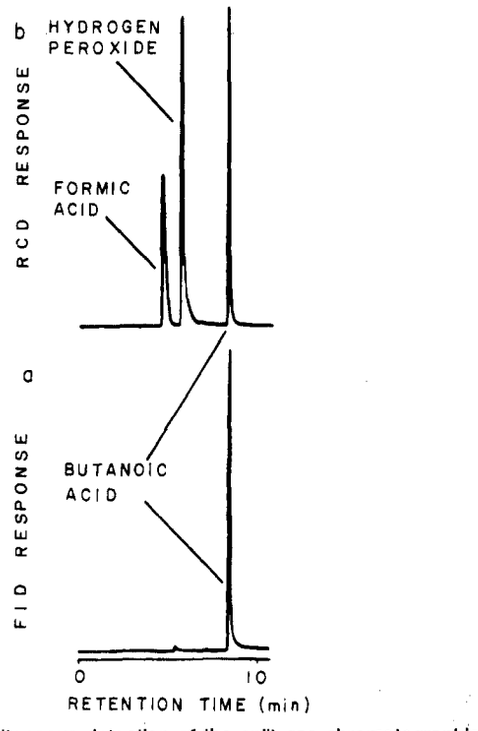


Figure 3. Simultaneous detection of the split gas chromatographic column effluent using a FID and RCD in parallel. The sample was an aqueous solution of formic acid, hydrogen peroxide, and butanoic acid. The lower chromatogram (a) shows that the FID only responds sensitively to the butanoic acid. The upper chromatogram (b) shows that the RCD responds sensitively to all three compounds and does not suffer interference from the solvent water. Column temperature was 40 °C for 1 min, programmed to 120 °C at 10 °C/min.

detectors are unable to respond sensitively.

Sensitivity of the RCD. The absolute response of several compound classes increased as the reaction bed temperature was increased from 150 °C to 500 °C. However, background noise was observed to increase exponentially through this same temperature region, presumably due to thermal decomposition of NO_2 to NO (*28*). An optimum heating mantle operating temperature of 400 °C was empirically chosen under the particular operating conditions (catalyst composition, bed dimensions, flow rates, and reaction chamber pressure) to maximize the signal to noise ratio. The actual temperature in the catalyst bed is approximately 50 °C lower than the heating mantle temperature, as indicated by imbedding a thermocouple in the catalyst bed temporarily. Also, at 350 °C to 400 °C the absolute response generated by most compounds which reduce NO_2 to NO was a maximum. Relative response ratios were determined at a heating mantle temperature of 400 °C. It should be emphasized that, under other operating conditions, lower or perhaps higher catalyst bed temperatures may give the best signal to noise ratio for a particular compound. Changing the catalyst bed temperature also affords a method of altering the selectivity of detection. At lower temperatures fewer compounds react rapidly with NO_2 at the gold surface.

Note Added in Proof. Recent experiments have shown that lowering the catalyst temperature allows highly selective detection of methanol in gasohol (*J. Chromatogr.*, submitted) and of BHT in jet fuel (*Chem. Eng. News* **1985**, June 24, 42).

Some compounds which gave poor response at normal operating temperatures produced measurable amounts of NO at reaction bed temperatures above 400 °C. Methyl esters and furans are examples of less reactive compounds. It appears that the reaction bed temperature can serve as an important parameter to tailor the selectivity of the RCD to

Table II. Relative Molar Response Factors for Selected Compounds

compound	RRF[a]	compound	RRF[a]
1-pentanol	0.66	benzaldehyde	0.57
1-hexanol	1.00	anisaldehyde	2.23
1-heptanol	1.38	*p*-tolualdehyde	0.72
1-octanol	1.93	5-nonanone	1.20
1-nonanol	1.95	4-methyl-2-pentanone	0.22
2-octanol	0.86	2,6-dimethylphenol	1.05
4-methyl-2-pentanol	0.25	aniline	1.52
tert-amyl alcohol	0.09	2,6-dimethylaniline	1.70
benzyl alcohol	0.36	1-octanethiol	0.41
2-phenylethanol	1.03	*tert*-butyl disulfide	1.19
3-phenylpropanol	1.53	cyclohexene	0.05
heptanal	1.00	naphthalene	2.16
octanal	1.62	1-methylnaphthalene	2.39
nonanal	2.20		

[a] Relative molar response factor = (RCD response, per mole of analyte)/(RCD response, per mole of 1-hexanol).

particular needs. All work reported here was performed with the reaction bed heating mantle at 400 °C, unless a lower temperature is specified.

Tolerance to Solvents and Principal Constituents of Sample Matrices. Relative response ratios for 27 representative reactive compounds determined by injection of standard solutions in various solvents are shown in Table II. A relative response of 1.00 was arbitrarily assigned to 1-hexanol. Relative molar response factors range from $<10^{-6}$ to 2.4. Primary and secondary alcohols respond well, but *tert*-amyl alcohol produced a much lower response, presumably because of the greater difficulty of oxidizing tertiary alcohols. Tests were made to determine whether representative common solvents might poison the catalyst. The response of the RCD to most of the analytes was virtually independent of solvent. However, compounds which eluted with the solvent (and which were not even detectable by FID due to large solvent peaks) showed a somewhat depressed response by RCD compared to injections of the same compound without the solvent. This effect is believed to be caused either by quenching of the NO chemiluminescence due to a high concentration of solvent vapor in the reaction chamber or by transient masking of the catalyst surface by the excess solvent, thereby inhibiting reduction of NO_2 to NO. Serious variations in response due to coelution of solvent can usually be avoided by using inert solvents or by altering chromatographic conditions. The effect of a depressed response can be minimized by calibrating with the same solvent used for the sample being analyzed, under the same conditions with the same sample size. Particularly attractive is the possibility of measuring volatile analytes coeluting with alkane or chlorinated alkane solvents such as hexane or methylene chloride, which do not produce a response with the RCD.

Table III is a list of compounds which give very low or no detectable response with the RCD. Only with direct injections of milligram quantities of these compounds was measurable response observed at 350 °C to 400 °C. This corresponds to a relative molar response factor (RRF) of approximately 10^{-5} to 10^{-6}, where

$$\text{RRF} = \frac{\text{(RCD response per mole of analyte)}}{\text{(RCD response per mole of 1-hexanol)}} \quad (8)$$

Direct injection of dilute standards in hexane was used to determine the minimum detectable amount (MDA) of a reducing agent. Typically 1.5 μL of a solution which contained about 1.5 μg of analyte was injected and this was split 50 to 1. Even with this first generation equipment, as little as 200 pg of 2,6-dimethylphenol (DMP) could be consistently detected at a signal to noise ratio of 2. Similar limits of detection were observed for 1-octanol, 5-nonanone, and 1-methylnaphthalene. The MDA is currently limited by the combined effects of background chemiluminescence arising from thermal decomposition of a minute amount of NO_2 on the heated surfaces of the catalyst bed, photomultiplier dark current, chromatographic peak shape, and reducing agents present as trace impurities in the various gases used. With refinements in the apparatus and detection system, it is reasonable to expect even better detection limits. It should be noted that at 400 °C, much larger amounts of NO than those observed would be expected if the system were at thermodynamic equilibrium. Care must be taken to avoid construction materials that can catalyze appreciable thermal dissociation of NO_2 to NO, so as to avoid high background signals. A commercially available RCD system has been developed that incorporates these features (*29*, *30*).

Table III. Compounds That Produce Very Low or No Detectable Response with RCD at 350-400 °C

compound	RRF
water	$<1 \times 10^{-6}$
dichloromethane	$<1 \times 10^{-6}$
pentane	$<1 \times 10^{-6}$
octane	$<1 \times 10^{-6}$
hexane	2×10^{-6}
2,2,4-trimethylpentane	1×10^{-6}
cyclohexane	1×10^{-6}
tetrahydrofuran	2×10^{-5}
2-methyltetrahydrofuran	2×10^{-5}
C_7 and C_9 to C_{14} *n*-alkanes	N.D.[a]
1,2-dichloroethane	N.D.
tetrachloroethylene	N.D.
oxygen	N.D.
nitrogen	N.D.
helium	N.D.
argon	N.D.
carbon dioxide	N.D.

[a] N.D., No detectable response was observed, and the RRF was not determined.

Linearity and Dynamic Range. The RCD response was linear with the experimental apparatus used in the present study from the limit of detection of 200 pg up to 100 ng for DMP. The NO pulse resulting from more than 100 ng of DMP was sufficient to saturate the photomultiplier tube currently in use, so the true upper limit of the range of detection possible with other light measuring arrangements has not been ascertained. Light emission from the NO/O_3 reaction is known to be linear over at least 5 orders of magnitude (*16*, *23*); however, the linearity of the catalyzed NO_2 reduction which is central to the RCD is not yet known beyond what is reported here. The intrinsic sensitivity of detecting NO by chemiluminescence upon reaction with ozone in state-of-the-art custom-made detectors allows one to measure <0.01 ppb of NO (*22*), so the potential sensitivity of the sensor, assuming background catalyzed dissociation of reagents can be minimized, is very promising. Repetitive injections of the same solution consistently produced the same magnitude of response, under identical instrument conditions, with a relative standard deviation that is typically less than 5%. The catalyst is surprisingly resistant to degradation and poisoning. This probably arises from the chemical inertness of gold and from the constant stream of a few parts per million of the strong oxidizing agent, NO_2, over the gold surface. Catalyst beds have been used for months without appreciable deterioration with a wide range of analytes being passed through them.

Registry No. DMP, 576-26-1; NO_2, 10102-44-0; H_2O_2, 7722-84-1; O_3, 10028-15-6; Au, 7440-57-5; ammonia, 7664-41-7; hydrogen sulfide, 7783-06-4; carbon disulfide, 75-15-0; sulfur dioxide, 7446-09-5; hydrogen, 1333-74-0; carbon monoxide, 630-08-0;

formaldehyde, 50-00-0; formic acid, 64-18-6; 1-pentanol, 71-41-0; 1-hexanol, 111-27-3; 1-heptanol, 111-70-6; 1-octanol, 111-87-5; 1-nonanol, 143-08-8; 2-octanol, 123-96-6; 4-methyl-2-pentanol, 108-11-2; *tert*-amyl alcohol, 75-85-4; benzyl alcohol, 100-51-6; 2-phenylethanol, 60-12-8; 3-phenylpropanol, 122-97-4; heptanal, 111-71-7; octanal, 124-13-0; nonanal, 124-19-6; benzaldehyde, 100-52-7; anisaldehyde, 50984-52-6; *p*-tolualdehyde, 104-87-0; 5-nonanone, 502-56-7; 4-methyl-2-pentanone, 108-10-1; aniline, 62-53-3; 2,6-dimethylaniline, 87-62-7; 1-octanethiol, 111-88-6; *tert*-butyl disulfide, 110-06-5; cyclohexene, 110-83-8; naphthalene, 91-20-3; 1-methylnaphthalene, 90-12-0; 2-pentanol, 6032-29-7; phenylacetaldehyde, 122-78-1; acetone, 67-64-1; butanone, 78-93-3; *N,N*-dimethylaniline, 121-69-7; 2-hexene, 592-43-8; 1-methylcyclohexene, 591-49-1; 1-nitropropane, 108-03-2; 2-nitropropane, 79-46-9; tetrahydrothiophene, 110-01-0; benzene, 71-43-2; toluene, 108-88-3; indole, 120-72-9; tetrahydrofurfuryl alcohol, 97-99-4; diethyl ethylphosphonate, 78-38-6; triethyl phosphite, 122-52-1; tri-*n*-butyl phosphite, 102-85-2; dibutyl phosphite, 1809-19-4; triethyl phosphate, 78-40-0; butanoic acid, 107-92-6; myrcene, 123-35-3; *p*-cymene, 99-87-6; limonene, 138-86-3; octanol, 111-87-5; neral, 106-26-3; geranial, 141-27-5; neryl acetate, 141-12-8; geranyl acetate, 105-87-3.

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Determination of Pore Accessibility in Silica Microparticles by Small Angle Neutron Scattering

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The size, surface area, and, in particular, the accessibility of pores in silica particles used in liquid chromatography have been studied by small angle neutron scattering (SANS). From SANS measurements on dry silica samples, values for the specific surface area are obtained and have been compared with BET measurements. Pore accessibility has been studied by saturating the samples with an H_2O/D_2O solution whose neutron scattering length density matches that of silica. Any residual scattering observed under this condition can be attributed to closed (unfilled) pores. Results are reported for silica particles with nominal pore size ranging from 5 to 33 nm. In addition, other applications of SANS related to the use of porous silica in chromatography and catalysis are discussed.

The physical structure of porous silica microparticles used in liquid chromatography is normally characterized by parameters such as the average pore size, specific surface area, and specific pore volume as determined by gas adsorption techniques (i.e., BET) or mercury porosimetry, for example. For microparticles with pores ranging in size from roughly 1 to 100 nm, small angle scattering of X-rays or neutrons provides an alternate means of characterizing the porosity which can potentially yield additional structural information not obtainable by these other techniques. For example, specific structural models for the pores, including their spatial organization and size distribution, can be tested by comparison with scattering measurements. Also, since both open and closed pores contribute to the small angle scattering, pore connectivity or accessibility can be investigated as well. This can be done, in principle, by comparing surface areas from scattering measurements with surface areas derived from nitrogen adsorption, which samples only the interconnected

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