# Gas chromatographic identification of interferences and their elimination in measuring total reduced sulfur gases

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**ABSTRACT** *A selective filter that is capable of eliminating positive interference in the coulometric measurement of ambient concentrations of total reduced sulfur gases has been successfully developed and field tested. Most of the interference was found to be caused by terpenes, which react with bromine, the active reagent in the coulometric titrators. Terpenes are given off by conifer trees in the natural environment as well as emitted in pulping and other wood-handling and lumber manufacturing operations.*

**KEYWORDS**
Coulometry
Development
Filters
Gas
Gas chromatography
Identification
Interference
Measurement
Selectivity
Test methods
Total reduced sulfur

## Introduction

Environmental control agencies require that industries that emit pollutants monitor them continuously, and this includes emissions of malodorous sulfur compounds generated in the kraft pulping process. These compounds are a mixture of hydrogen sulfide ($H_2S$), methyl mercaptan ($CH_3SH$), dimethyl sulfide ($(CH_3)_2S$, and dimethyl disulfide ($(CH_3)_2S_2$. As a group, these compounds are referred to as total reduced sulfur (TRS) gases. They are presently monitored with instruments based on the principle of coulometry in certain Canadian mills, but not so in the United States. Two instruments used are the Barton Titrator, which is widely used for point source measurements, and the Philips $SO_2$ monitor [fitted with a filter that passes $H_2S$ and mercaptans but removes sulfur dioxide ($SO_2$), ozone ($O_3$) and nitrogen dioxide ($NO_2$)] which is commonly used for ambient concentrations. The sulfur compounds react with bromine in a titration cell, the amount of bromine consumed being a measure of their concentrations. Unfortunately, other non-sulfur-containing organic compounds that are not regulated have been found (*1*) to react with bromine, thereby causing positive interference and erroneously giving higher TRS concentrations than the actual amounts present. Such positive errors in ambient TRS measurements can lead to unjustified regulatory actions being taken against a pulp mill. The mill may be forced to install unnecessary and expensive pollution control equipment.

An idea as to the type of gases emitted by pulping and papermaking operations can be gained from earlier research works. In 1970, Thoen and Nicholson (*2*) carried out a qualitative study of gaseous compounds emitted from the kraft pulping process. Using an infrared technique, they identified at least 12 compounds, including methane, methanol, ethylene, acetone and "turpentine" emitted by a kraft recovery furnace burning black liquor obtained from the pulping of Douglas-fir, alder, and red cedar chips. Indications of the possible type of gaseous compounds emitted from an overloaded kraft furnace can be obtained from the laboratory work of Feuerstein *et al.* in the pyrolysis of spent pulping liquors (*3*). They reported that 80% of total sulfur in black liquor was converted to $H_2S$ and $CH_3SH$ at pyrolysis temperature of 900°C. Other workers (*4-6*) found compounds that belonged to the following groups: terpenes, sulfides, alcohols, ketones, ethers, and phenols from analyses of volatiles from con-

densates and such. Wilson and Hrutfiord (*6*) listed 40 specific compounds identified in kraft pulp mill condensates. Most of these compounds were determined qualitatively and were found to include terpenes, methanol, ethanol, acetone, guaiacol, and organic sulfides.

Up to now, no significant data or knowledge were available on interference caused by certain compounds in the monitoring of TRS both in relatively high (source) and low (ambient) concentrations, hence no knowledge existed in eliminating them either. Investigations of interferences of other organic compounds in TRS measurements were carried out by the Environmental Protection Agency (U.S. EPA) in developing methods 15 and 16, in the early 1970s. Our efforts in this direction were due to our earlier findings (*1*) and the belief that identifying and possibly removing these interference-causing compounds would benefit not only the pulp and paper industry but also help the regulatory agencies by obtaining more accurate results than were heretofore possible with available TRS monitors.

## Results and discussion

### Response of coulometric titrators to gaseous organic compounds

Although information exists on component analysis of exhaust gases from spark ignition and diesel engines (*7*), the response of the Barton Titrator to these gases was unknown. In our limited tests, analysis of exhaust gases from both types of engines (after warm-up times of 4-5 min before sampling) gave negligible Barton cell response, indicating insignificant interference from exhaust gases of both types of vehicles at least in these tests.

The response of the Barton Titrator to various organic compounds in terms of equivalent concentrations of hydrogen sulfide is shown in **Table I.** These particular compounds were chosen for the study because they belonged roughly to two groups of compounds that were known to be present, or suspected to be, around pulp mills. One group consisted of low molecular weight compounds that exist in the gaseous phase, whereas the other consisted of liquids that belonged to the heavier aromatic and terpene families. The last column of Table I shows that the Barton response is greatest to terpenes like α-pinene and anethole, closely followed by that to α-phellandrene, β-pinene and myrcene. None of the low molecular weight gaseous compounds containing less than seven carbon atoms reacted significantly with bromine in the titration cell. This study indicated that most of the interference could be expected to come from terpene compounds that are given off naturally by evergreen trees and from some parts of a pulp mill, such as blow pits, washer hoods, and vents.

**I.** Response of Barton Titrator to some organic compounds

| *Compound* | *Approximate concentration present, ppm* | *$H_2S$ equiv., ppm* | *ppm $H_2S$/ppm organic compound* |
|---|---|---|---|
| Methane | 40,000 | 0.9 | 0.000 |
| Acetylene | 40,000 | 1.3 | 0.000 |
| Ethylene | 4,000 | 23.2 | 0.008 |
| Ethane | 40,000 | 1.3 | 0.000 |
| Methanol | 33,100 | 0.0 | 0.000 |
| Ethanol | 15,500 | 1.7 | 0.000 |
| Acetone | 89,300 | 114.4 | 0.001 |
| Diethylether | 69,900 | 11.2 | 0.000 |
| Benzene | 10,850 | 1.7 | 0.000 |
| Toluene | 4,000 | 1.3 | 0.000 |
| Xylene | 1,860 | 0.9 | 0.000 |
| α-Pinene | 2,900 | 594.0 | 0.204 |
| d-Limonene | 1,380 | 74.0 | 0.054 |
| Terpinoline | 450 | 2.6 | 0.006 |
| d-Fenchone | 460 | 23.2 | 0.050 |
| α-Terpineol | 80 | 1.6 | 0.020 |
| Ethylbenzene | 5,800 | 0.9 | 0.000 |
| p-Cymene | 1,400 | 0.9 | 0.000 |
| α-Phellandrene | 940 | 150.8 | 0.160 |
| Anethole | 40 | 7.7 | 0.193 |
| Linalool | 195 | 1.7 | 0.009 |
| Guaiacol | 74 | 0.0 | 0.000 |
| Cineole | 1,230 | 3.4 | 0.003 |
| Myrcene | 1,410 | 207.0 | 0.147 |
| β-Pinene | 2,755 | 405.0 | 0.147 |
| Vanillin (solid, head space) | Unknown | 0.0 | |

**II.** Filtering properties of decanol and DMF in the removal of gaseous α-pinene and sulfur compounds (Approx. concentrations, (ppm); Net recorder divisions of Barton Titrator)

| | *$H_2S$ (7.5)* | | *$CH_3SH$ (9)* | | *$(CH_3)_2S$ (13)* | | *α-Pinene (conc. unknown)* | |
|---|---|---|---|---|---|---|---|---|
| *Filter used* | *Direct* | *Through filter* | *Direct* | *Through filter* | *Direct* | *Through filter* | *Direct* | *Through filter* |
| Decanol | 9.0 | 9.0 | 9.0 | 9.0 | 7.0 | 7.0 | 13.0 | 0.0 |
| DMF | 10.0 | 10.0 | 9.0 | 7.0 | 7.0 | *[a] | 20.0 | 0.0 |

[a]Operating problems (blockage)

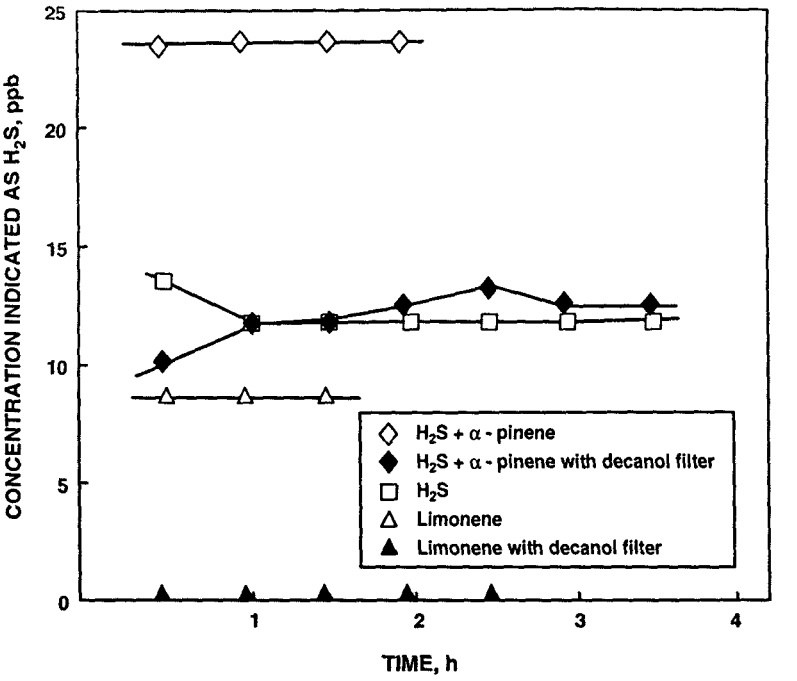
### Assessment of filter materials

The responses of the Barton Titrator and flame ionization detector (FID) to α-phellandrene, myrcene, and α-pinene were significant when sensed directly, but negligible when the compounds were passed first through

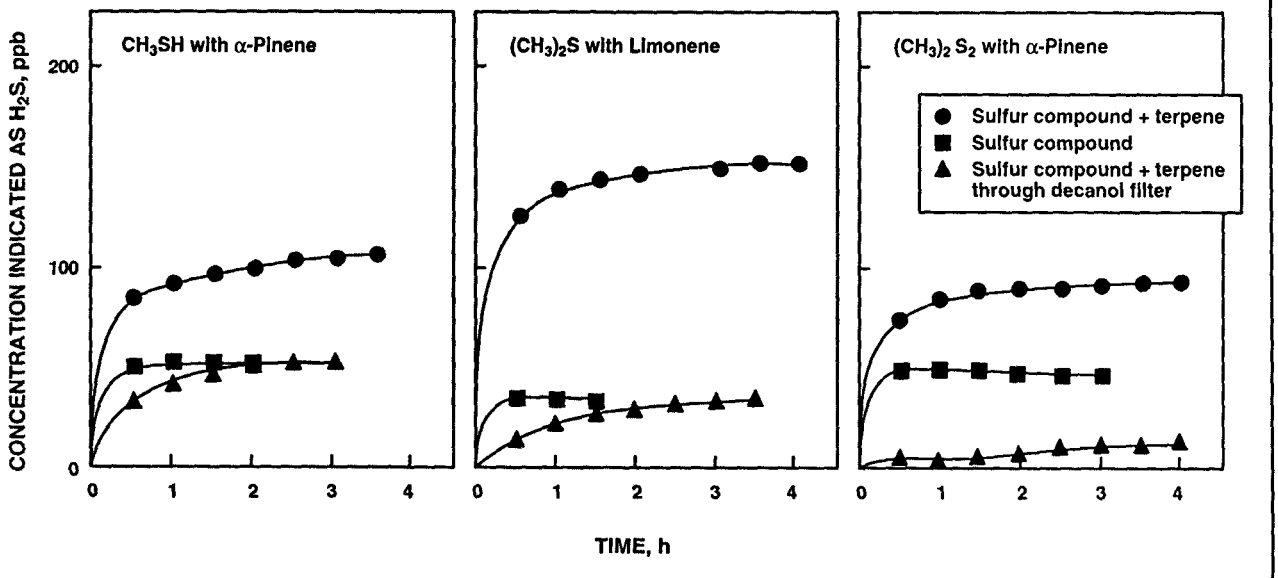
**III.** Recovery of gaseous α-pinene and sulfur compounds passed through DMF or decanol filters

| Compound | Approx. conc. present, ppm | Recovery, % | |
|---|---|---|---|
| | | Decanol | DMF |
| $CH_3SH$ | 117 | 100 | 66 |
| $(CH_3)_2S$ | 70 | 98 | 35 |
| $(CH_3)_2S_2$ | 38 | 28 | 0 |
| α-Pinene | 38 | 0 | 8 |

**1.** Removal of α-pinene and limonene by decanol filter in the presence of $H_2S$




**2.** Removal of α-pinene and limonene by decanol filter in the presence of $(CH_3)_2S$ and $(CH_3)_2S_2$



either dimethyl formamide (DMF) or decanol. This indicated near total removal of the three terpene compounds by the two filtering media tested. The results of a study involving $\alpha$-pinene (the most abundant terpene) and three sulfur compounds, summarized in **Table II**, confirmed, however, that decanol was superior to DMF in terms of selectivity. The results of another recovery test performed with individual TRS and other organic gases passed through either DMF or decanol at the flowrate of 250 mL/min to a FID are presented in **Table III**.

The decanol filter totally removed interfering organic compounds found in and around kraft pulp and paper mills. It did this selectively, leaving the sulfur compounds to pass through without any significant loss [except $(CH_3)_2S_2$] or change in their compositions.

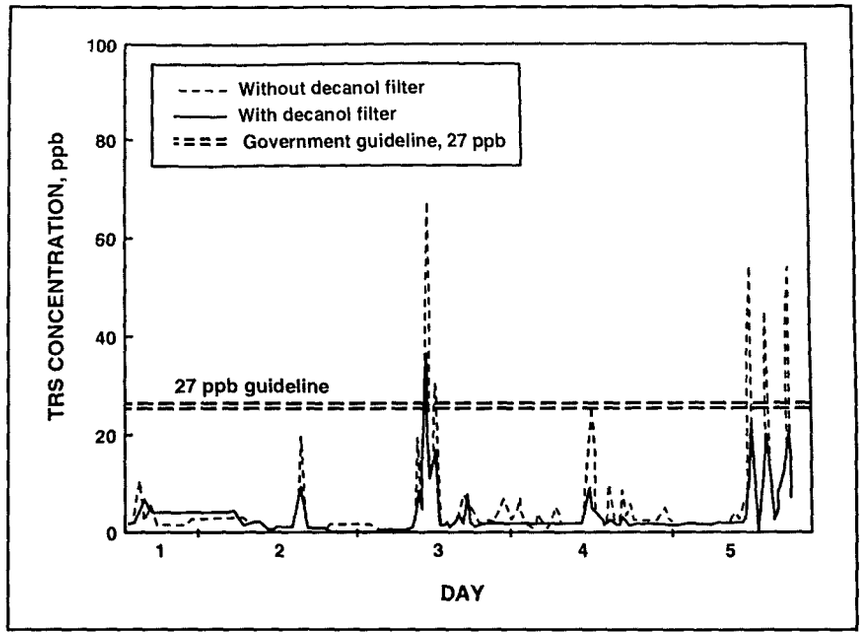
The partial recovery of $(CH_3)_2S_2$ should have very little effect on the accuracy of ambient TRS readings since, generally, it is either absent or represents not more than 10% of TRS emissions from typical kraft pulp mill operations (*8*).

The decanol filter was also tested as a selective agent for the removal of limonene and $\alpha$-pinene from a synthetic mixture containing $H_2S$ at ambient concentrations (10 to 25 ppb). The mixtures were prepared using permeation tubes.

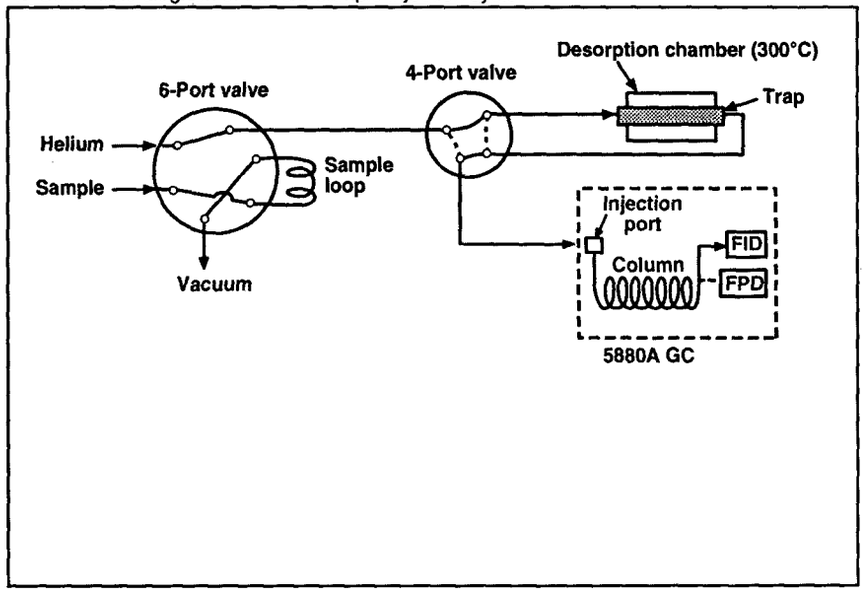
The results of the tests shown in **Fig. 1** indicate very clearly that the filter absorbed limonene and $\alpha$-pinene completely. The reading obtained with a mixture of $\alpha$-pinene and $H_2S$, after being stripped of its $\alpha$-pinene component, was the same as that obtained with $H_2S$ alone prior to mixing.

On another occasion, the filter was tested in order to verify its selective performance in separating non-sulfur-containing organic compounds from the organic components of TRS. The results obtained are shown in **Fig. 2**. It was confirmed that the filter selectively absorbed both $\alpha$-pinene and limonene from mixtures with $CH_3SH$, $(CH_3)_2S$, and $(CH_3)_2S_2$ allowing the sulfur gases to pass through [$(CH_3)_2S_2$ only partly] after about a 2-h conditioning period.

**3.** Comparative results from two Philips TRS analyzers, with and without decanol filter




**4.** Schematic diagram of the GC sample injection system




### Field testing the decanol filter

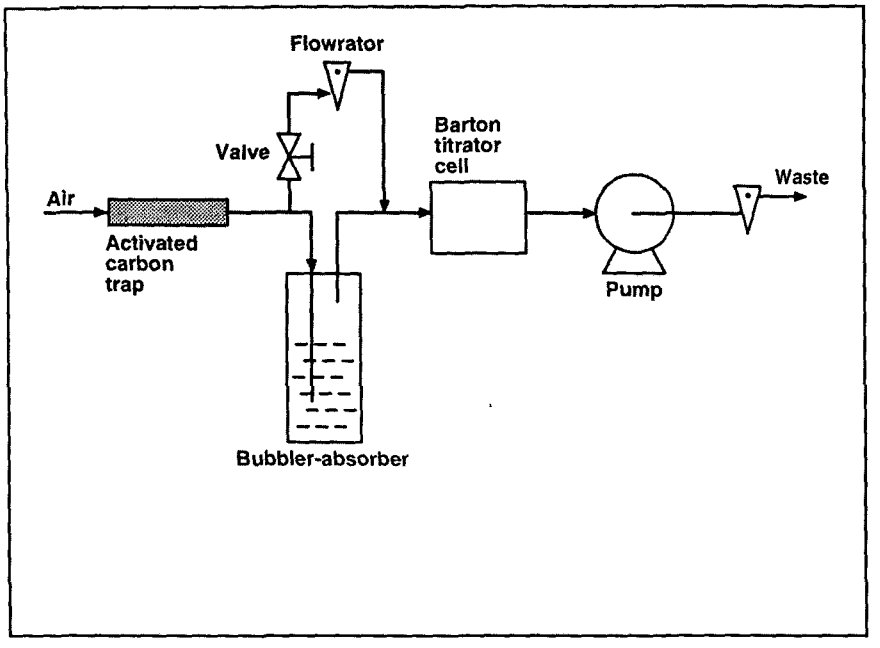
**Figure 3** shows the comparative results obtained with the two Philips TRS analyzers (with and without decanol) in the field test. The instrument equipped with the decanol filter responded lower than that without, particularly during peak emission periods. Out of five apparent violations (exceeding the government guidelines of 27 ppb), only one appeared to be real. In this test, the filter operated well for more than one week.

From 13 composite samples collected of the ambient atmosphere outside the TRS-monitoring station during the above-mentioned tests, 3-24 compounds per sample were detected by the GC/FID procedure. Of these, some were aromatics while others were terpenes that interfere in TRS measurements.

## Conclusions

Coulometric TRS analyzers (with bromine reagent), used by regulatory

**5.** Apparatus used to study response of Barton Titrator to vapors of organic liquid compounds




**IV.** GC conditions used in gas analyses with DB-1 column

| GC Condition No. | 1 | 2 |
|---|---|---|
| Sample: | | |
| Volume, mL | 0.5 | 5 |
| Split ratio | 1:100 | 1:25 |
| Gas flow rates: | | |
| Helium carrier pres., kPa | 256.5 | 256.5 |
| Linear velocity, cm/s | 49.8 | ... |
| Air, mL/min | 450 | 450 |
| Hydrogen, mL/min | 30 | 30 |
| Oven temperature program: | | |
| Initial temp., °C | -50 | 30 |
| Initial hold time, min | 4.5 | 4 |
| Rate of increase, °C/min | 30 | 30 |
| Final temp., °C | 175 | 175 |
| Final hold time, min | 20 | 20 |

Temperature of injection port and detector (FID) were maintained at 175 and 200°C, respectively.

agencies and some mills, have an inherent positive bias due to their responding to compounds other than TRS. Terpenes in particular are a significant source of error because they react with bromine and are found in abundance both naturally and in gaseous emissions from pulp mills. The use of a decanol filter eliminates this positive interference from terpenes and other compounds reacting with bromine. The partial recovery of $(CH_3)_2S_2$ should have very little effect on the accuracy of ambient TRS readings since, generally, it is either absent or represents not more than 10% of TRS emissions from typical kraft pulp mill operations. The filter can be inserted into present instrument sampling lines without difficulty, requiring very little attention or maintenance.

## Experimental

### Apparatus and materials

Hewlett Packard Model 5880A gas chromatograph (GC) equipped with a FID, Hewlett Packard Model 5985A GC/Mass Spectrometer (MS): with a 5840A GC. Two stainless steel 4- and 6-port valves from Valco Instruments Co. were incorporated into the sample injection system without disturbing the septum-equipped injection port of the GC. See **Fig. 4.**

Both Tedlar and Teflon (Cole Parmer Inst. Co.) bags in 30 × 30 cm sizes were used for sampling. The former came with dark opaque covers, the latter did not. Also used were 60 m × 0.32 mm ID fused silica capillary column Durabond 60W with bonded DB-1 phase and film thickness of 1 μm (Chromatographic Specialties, ON) and an ITT Barton Process Instruments Model 400 Titrator with control and titration cell modules. The latter held about 600 mL of 17% hydrobromic acid (HBr). Model PW 9700 $SO_2$ Monitor equipped with a selective filter for $SO_2$, $O_3$ and $NO_2$ (Philips Electronics, ON). A mixture of $H_2S$, $CH_3SH$, $(CH_3)_2S$, and $(CH_3)_2S_2$ was added to nitrogen, each in the 2- to 10-ppm concentration range, in an aluminum cylinder. At times, permeation tubes containing these gases were also used, allowing generation of lower concentrations.

A synthetic non-sulfur-containing gas mixture consisting of methane ($CH_4$), acetylene ($C_2H_2$), ethylene ($C_2H_4$), ethane ($C_2H_6$), propylene ($C_3H_6$), propane ($C_3H_8$), methanol ($CH_3OH$), acetone ($CH_3COCH_3$), and benzene ($C_6H_6$) in a cylinder of nitrogen was used. Each component gas in the cylinder was in the 250- to 500-ppm concentration range. Also used were permeation tubes containing α-pinene and limonene and cylinders of nitrogen with additions of α-phellandrene, myrcene and α-pinene.

The filter materials tested or screened were inorganic, organic, and polymeric compounds, both in liquid and solid forms. They included activated carbons, cellulose pulps of hardwoods and softwoods, cotton wool, Carbosieve B, Filtrasorb 200, Tenax GC with Carbosieve B and G, Molecular Sieves 3A and 5A, dimethyl formamide (DMF), and decanol. The solid filter materials were packed in 40-cm long and 0.6-cm ID glass tubes and, later, in stainless steel tubes or traps, as described elsewhere (*9*). The liquids were placed in bubbler-absorbers.

## Procedures

**Response of coulometric titrators to gaseous organic compounds.** In this screening study, a Barton Titrator was used without an oxidation furnace (used to convert TRS to sulfur dioxide). The sample gas was drawn through the titration cell at a rate of 250 mL/min by means of a peristaltic pump. Vapors of some low-boiling liquid compounds used in these tests were obtained by bubbling "zero" air, at room temperature, through the liquid compounds, as shown in **Fig. 5.**

**Gas chromatographic analysis.** Two GC conditions used in these tests are listed in **Table IV.**

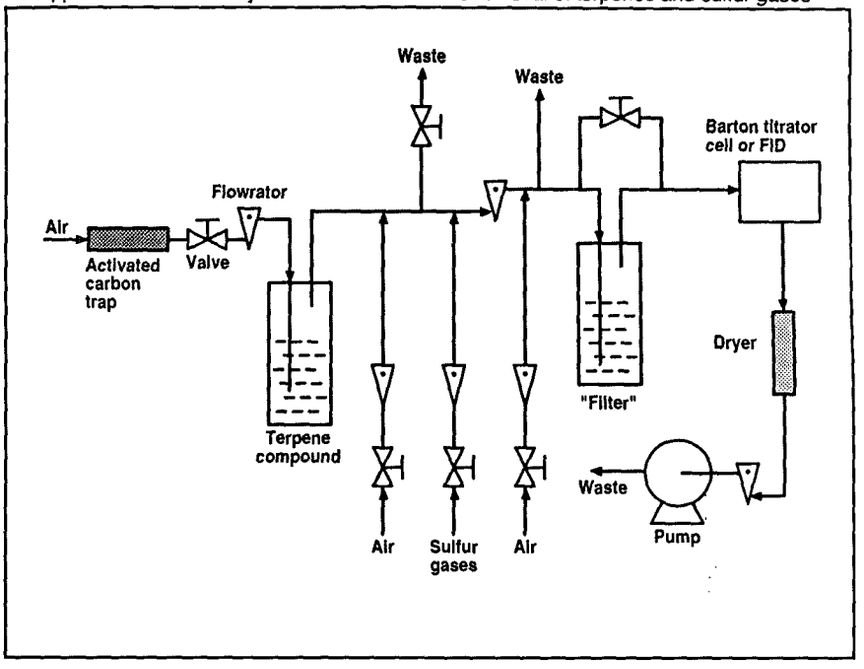
**Analysis of source and ambient gases from a pulp mill.** Gas samples from a hardwood kraft pulp mill were collected in Tedlar bags and "traps" (*9*) and analyzed with GC/FID and GC/MS. The traps were used mainly to collect ambient samples. Any point-source samples collected in traps were diluted before analysis. The contents of the traps were thermally desorbed and analyzed using the DB-1 separating column with both the GC/FID and the GC/MS procedures. The GC conditions used were as mentioned under conditions No. 1 and 2 (Table IV), respectively. In the case of the GC/MS analyzer, a small part (3 to 8 cm) of the separating column soon after the injection port was immersed in a beaker containing dry ice with acetone (-70°C) for 1 min before the start of analysis. This was done in order to concentrate the sample into a "slug" that would reduce peak broadening.

**Filtering terpene vapors with various materials.** Of the many liquid and solid reagents screened as potential "filters" the two most promising were found to be decanol and dimethyl formamide. The criteria used for the evaluation was selectivity, i.e., the ability of the substance to quantitatively absorb and hold all bromine-reacting non-sulfur-containing organic compounds while allowing all sulfur gases to pass through. Model terpene-type compounds found in kraft pulp mill emissions and yielding strong responses on coulometric titrators, were used in these tests. Gases from cylinders containing 15, 17.5 and 17.5 ppm of α-phellandrene, myrcene and α-pinene, respectively, were passed individually through solutions of either DMF or decanol at 250-mL/min flowrates and the exiting gases led to Barton and FID sensors. It was found that the filters needed preconditioning for up to 2 h with the sample gas to be analyzed.

A mixture of α-pinene with three sulfur compounds was used to further test the two filter materials with the apparatus as shown in **Fig. 6.** The scrubbing media were evaluated one at a time by passing the gases individually through the Barton cell or an FID directly and after passing through the medium placed in a bubbler-scrubber.

**Testing decanol filter at a government TRS-monitoring station.** Initially, synthetic gas mixtures were prepared from permeation tubes as

**6.** Apparatus used to study "filter" solutions for the removal of terpenes and sulfur gases




**V.** Analyses of source samples from a kraft pulp mill with GC/FID and GC/MS

| *Sample location* | *Bag* | *Trap* | *GC/FID Compd. detected* | *GC/MS Compd. detected* |
|---|---|---|---|---|
| Recovery furnace | | ✓ | Methane<br>Acetone<br>Ethanol<br>Benzene<br>Linalool<br>Unknowns (7) | Acetone, carbon disulfide, benzene, dimethyl disulfide, 2-butanone, methylene chloride, hexane, chloroform, trichloroethane, methyl ethyl benzene, dichlorobenzene, toluene, ethylbenzene, xylene, benzaldehyde, o-ethyl toluene, triethyl benzene, dimethyl ethyl benzene, unknowns (9) |
| Black liquor oxidizer | ✓ | | Acetone<br>Dimethyl sulfide<br>Dimethyl disulfide<br>Unknowns (4) | Methanol, methyl mercaptan, ethanol, acetone, dimethyl sulfide, dimethyl disulfide, benzene, 2-butanone |
| Lime kiln | | ✓ | Methane<br>Propylene<br>Benzene<br>Dimethyl disulfide<br>Toluene<br>Xylene<br>Unknowns (18) | Ethanol, acetone, dimethyl sulfide, benzene, dimethyl disulfide, toluene, xylene, methyl acetate, hexane, acetic acid, unknowns (7) |

**VI.** Analyses of ambient samples from a kraft pulp mill with GC/FID and GC/MS

| Sample location | Bag | Trap | GC/FID Compd. detected | GC/MS Compd. detected |
|---|---|---|---|---|
| Government TRS-monitoring station | | ✓ | Methane<br>Methyl mercaptan<br>Diethyl ether<br>Dimethyl sulfide<br>Benzene<br>Toluene<br>Xylene<br>α-Pinene<br>Camphene<br>(+)-3-carene<br>Linalool<br>Unknowns (11) | |
| Around the mill | | ✓ | | Acetone, benzene, hexane, 1-3-butanediol, 2-butanone, methylene chloride, cyclohexane, trichloro ethylene, toluene, tetrachloro ethylene, xylene, α-pinene, benzaldehyde, camphene, methyl ethyl benzene, *o,m*-cymene, *o*-allyl toluene, unknowns (10) |

**VII.** Quantitative analyses of gaseous compounds detected in work areas of a kraft pulp mill

| Compd. | Approximate Concentration, ppb: Digester area | BS[a] washer | Recovery area | Scrubber area | Woodroom |
|---|---|---|---|---|---|
| α-Pinene | 2467 | 608 | 44 | 72 | 433 |
| β-Pinene | 256 | 181 | 11 | 19 | 367 |
| Cineole | N.D. | 86 | 17 | N.D. | N.D. |
| Linalool | 19 | 17 | 17 | N.D. | N.D. |
| Myrcene | 69 | N.D.[b] | N.D. | 8 | 28 |
| α-Phellandrene | 25 | N.D. | N.D. | N.D. | 8 |

[a]BS = brown stock
[b]N.D. = not detected

sources of sulfur and organic gases, using activated carbon-filtered air as carrier. The mixtures were then directed one at a time to a Philips TRS analyzer after passing through the decanol filter. This was done in order to verify the total removal of organics by decanol and to obtain a calibration factor for $H_2S$, the predominant component of TRS. The calibration factor was later used to quantify unknown concentrations of TRS compounds (as $H_2S$) encountered in mill emissions.

The decanol filter was tested on three separate occasions at a government-owned mobile TRS-monitoring station situated about half a mile from a hardwood kraft pulp mill. Two Philips TRS analyzers were available, one for routine use by the government and the other for our research purposes. The same sample air was divided and analyzed simultaneously with the two instruments. The routine analyzer had a sample gas intake rate of 157 mL/min, the other 145 mL/min passing through the bubbler (containing 70 mL of decanol) before analysis. At the time of analysis, 2-L air samples were also collected outside the station in "traps" for later analyses with GC/FID system at our Institute in order to see what types of compounds existed in the sample air. The GC conditions used to analyze the trapped samples were the same as those described under condition no. 1 (Table IV).

## Preliminary screening analyses

During the early part of the project, we analyzed source and ambient gases from a pulp mill in order to identify all gases being encountered. The results obtained from the kraft pulp mill with GC/FID and GC/MS are shown in abbreviated **Tables V** and **VI**, respectively. As expected, the FID detector did not respond to $H_2S$ but did to the presence of $CH_3SH$, $(CH_3)_2S$, and $(CH_3)_2S_2$ in some of the samples. Many of the peaks detected were identified by their retention times matched to those of standard, model compounds. A GC/MS system was also used to confirm and to identify a larger number of compounds detected. **Table VII** shows quantitative analyses of ambient gases detected inside work areas of the mill. The relative GC response factors for each of the compounds was arbitrarily assumed to be equal to that of benzene for which a calibration curve was generated.□

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