

# Early Detection of Fire by Analysis of Smoldering Odor

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## ABSTRACT

The time honored methods of fire detection have depended upon, or been derived from, the four human senses of sight, sound, touch, and smell, each of which has advantages and disadvantages determined by its characteristics. Detection by smell depends upon the remarkably sensitive response of the olfactory nerve to vapors produced by the thermal decomposition of the fuel or of nearby materials which may or may not be combustible. It has the great advantage of being able in principle to detect a fire in its very early stages, long before it produces enough heat, light, sound, or smoke to produce a response by the other senses. This report describes the results of some preliminary experiments on the detection of combustion-produced vapors by two different kinds of "artificial noses" which have shown promising sensitivity. One depends upon the change in electrical conductivity of a thin oxide layer when it is exposed to vapors from thermal decomposition of cellulose. The other depends upon the mass spectrometric analysis of those vapors.

**KEYWORDS:** The early stage of fire, detection, odor sensor, smoldering odor, levoglucosan, cellulose, polymer, GC-MS, thermal analysis, thin film sensor, thermal decomposition products, mass spectrometry

## INTRODUCTION

Human recognition and/or realization of the existence of a fire can be achieved by sight, by sound, by odor and by touch (i.e. the skin's ability to sense temperature changes). Each of these abilities has its particular characteristics. Thus, fires that are large enough can be detected at great distances by their luminosity (especially at night) and/or the smoke that they produce (especially in daylight). The odor resulting from vapors due to thermal decomposition from very small fires, even from smoldering before ignition occurs, can be detected by one's sense of smell if air currents carry those vapors to his or her nose. Noise generated by a reasonably vigorous fire can be heard even when structures of some sort shield the observer from any radiation or odiferous vapors. As illustrated in FIGURE1, statistical data indicate that on average in practice 54 % of fires are detected by sight, 16 % by smell, and 14 % by sound(1). Even so, the sense of smell probably comprises the most versatile detection means because of its very high sensitivity and its ability to respond to vapors that are produced during the very early stages of an incipient fire, often long before it becomes visible and audible enough to have caused substantial damage(2,3). Moreover, a very large fraction of common materials of construction contain organic materials, which can produce odiferous vapors in the very early stages of a fire, long before the onset of flame or visible smoke. For these and other reasons vapor detection constitutes a most attractive means for the early detection and warning(4).

Unfortunately, it is not feasible to provide continuous detection over large areas for long periods of time by taking advantage of the keen sense of smell of which many living organisms, e.g. dogs, are capable. Such "living detectors" require a lot of "maintenance" and have a limited

duty cycle because they are very subject to fatigue. Consequently there has long been great interest in developing inanimate devices that can sense the odors from combustion at very low concentrations(5). The now commonplace smoke detectors can in some sense be considered as "mechanical noses" because they are activated by vapors carrying fumes containing very small particles that attenuate a flux of ions to a detector. Such vapors also usually contain

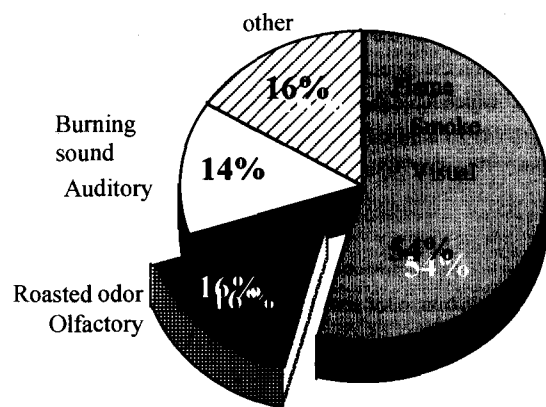


FIGURE1.  
Recognition of fires by senses of human

odiferous compounds detectable by smell. Thus one could consider a smoke detector as a sort of mechanical nose even though its activation is by a physical blocking or scattering of an ion flux rather than by a chemical interaction between a particular molecular species and the olfactory nerve. Also to be realized is that the fume particulates that do the blocking are not produced until the source material has reached a very high temperature. Thus, smoke detectors provide early warning only in the sense that they alert people to a fire that has already started but is far enough away so that those who hear its alarm have an opportunity to escape or even to locate and extinguish it before it spreads out of control. A more desirable detector would sense vapors from thermal decomposition at very early stages of an incipient fire, before the local temperature reached high values.

Because many of the materials that are fuel for fires contain cellulose, the thermal decomposition of this very common substance and analysis of the resulting vapors have been investigated at great length. The final products of complete combustion of cellulose comprise  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{O}$ , none of which have any odor and all of which are almost omnipresent in the atmosphere. Fortunately, combustion is never complete so that all fires involving cellulosic material produce substantial quantities of intermediates(6) that have enough chemical complexity to be distinguishable from the common atmospheric components as well as detectable by odor or an appropriate sensor. FIGURE2 shows a schematic representation of the thermal decomposition cellulose(7). Relatively simple reactions give rise to substantial quantities of the compound levoglucosan when cellulose is heated above about  $200^\circ\text{C}$ . In the present study preliminary experiments were carried out on the detectability of levoglucosan by a novel thin-film sensor as well as by mass spectrometry. Some experiments were also done with the common plastic(8,9) polyvinyl chloride(10,11).

## MATERIALS, APPARATUS AND PROCEDURES

### Materials

Cellulose samples comprising fibers,  $7\ \mu\text{m}$  in diameter (PHM06) were from Asahi Chemicals. Polyvinylchloride (PVC) (700D), with a density of  $0.54\text{g/ml}$  and an average degree of polymerization of 1020 was obtained from TOSO and levoglucosan hydroxyacetone  $\alpha$ -angelicalactone furfuryl alcohol pyruvic aldehyde 5-methylfurfuroyl diacetyl furfural and furan from Merck.

### Apparatus

#### GC-MS

Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC-MS) was carried out with a Hewlett Packard HP8590 type III system connected to a drop type pyrolyzer (Frontier Laboratory Py-2010D). The sample inlet temperature was  $320^\circ\text{C}$ . The split ration was 40:1. The GC column

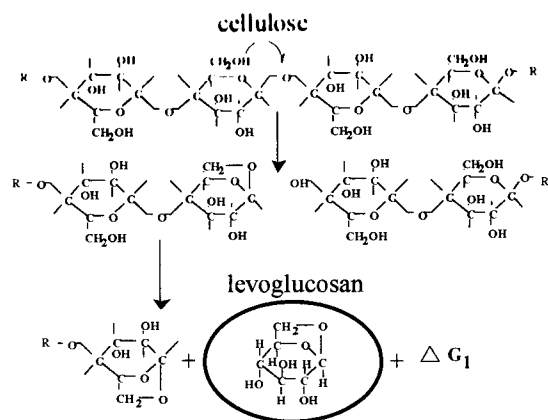


FIGURE2.  
Pyrolysis mechanism of cellulose

TG-DTA 2000S modes. Other TG-MS analyses were obtained with a Skimmer Type TG-MS made by a Netzsch Instrument (409C/403/5E).

#### Odor sensor

The thin film type semiconductor sensor comprised a thin (100 nm) layer of SnO<sub>2</sub> deposited on an aluminum substrate. A layer of platinum sputtered on the underside of the substrate served as a resistance heater to maintain the sensor at a desired temperature, 350°C in these experiments(12). The electrical resistance of the SnO<sub>2</sub> layer decreased upon exposure to vapors from decomposition products. The sensor was placed in a stainless steel enclosure (Odor Testing Box). A sample of material of known weight, e.g. 1~5mg of cellulose, was placed on a small aluminum pan whose temperature was raised at a desired rate in the stainless steel enclosure. The resistance of the sensor was recorded as resulting pyrolysis vapors flowed into the box against the temperature of the sample.

#### Odor Testing Box

The relation between the odor sensor output and the concentrations of thermal decomposition products was analyzed in the stainless steel odor testing box of 27 x 27 x 22cm shown in FIGURE3. This box had a fan, a heater underneath the aluminum sample holder and odor sensors. A small amount of pure sample was placed in the sample holder and the temperature of the sample was raised to about 80% of its boiling point. Levoglucosan and angelicalactone were injected as calculated amount of 1.0wt-% aqueous solution into hot sample holder through the 1mm diameter of pinhole in the wall near the sample holder and were vaporized. The resistivity of the odor sensor was measured by changing the concentrations of samples to control odor concentration

was an Ultra alloy-Py-2 column, 30 mm in length and 0.25 mm in diameter. Temperature programming comprised an initial minute at 40°C, followed by an increase of 25°C/min up to 340°C. The carrier gas was helium flowing at 40 mL/min.

#### TG-MS

Some Thermogravimetric Analysis Mass Spectrometry (TG-MS) was carried out with a Capillary type TG-MS instrument made by Mac Science Ltd. Analyses were performed in both the TG-DTA-MS and the

in the box. Both solid samples and the solution samples were vaporized by heater in pan. In order to avoid the influence of water vapor, the sensor was kept at about 300°C by thin film Pt heater Mass Spectrometer with differential pumping system and capillary was used to double-check the concentrations of vapors in the box. Ethylalcohol was used as a standard vapor to examine the vapor concentration in this box.

#### APCI-MS

Analysis of pyrolysis vapors was carried out by Atmospheric Pressure Ionization Mass Spectrometry (APCI-MS) with a UB-240 instrument from Hitachi Tokyo Electronics, LTD. Nitrogen (99999 grade) was the carrier gas. The sample was placed in a silica capillary with an inside diameter of 5 mm and surrounded by a heater at RT for 24 hours to achieve degassing and drying. The heater temperature was then raised stepwise to values of 40, 60, 80, 100, 125, 150, 175, 200, 225, 250, 275, 300 and 500°C. The temperature at each step was maintained for 10 minutes to reach a steady state before an APCI mass spectrum was obtained on the nitrogen exiting the heated sample.

#### ESI-MS

Analyses were also carried out with a Thermoquest TSQ-700 mass spectrometer having an Electrospray Ion (ESI) source(13). Vapors from the pyrolysis unit were bubbled through 50 mL of a 50-50 methanol water mixture and trapped. Small quantities of the resulting solution of pyrolysis products in methanol were then introduced into the ESI source of the TSQ-700 at a flow rate of about 2μL/min to obtain an ESI-MS spectrum of the pyrolysis products that had been dissolved.

## RESULTS AND DISCUSSION

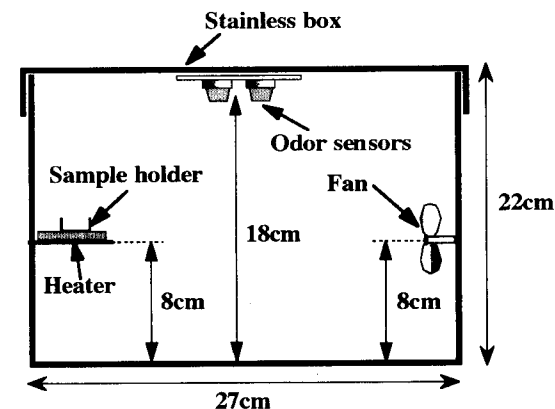


FIGURE3.  
Schematic diagram of odor testing box.

FIGURE4 shows curves resulting from Thermogravimetric (TG) analysis (left hand ordinate) and differential Thermogravimetric (DTG) analysis (right hand ordinate) of a 5.0 mg sample of cellulose in atmospheres of both nitrogen and a "synthetic air" comprising an 80-20 mixture (by volume) of nitrogen and oxygen. The heating rate was 10°C/min. Clearly the thermal degradation reaches

a measurable rate at about 250°C. Between 250 and 325°C the "crystalline" cellulose "melts" with random breaking of the main polymer chains and dehydration reactions occurring simultaneously. From 325 to 350°C dehydration of monomer units results in the formation of levoglucosan and water vapor whose departure is indicated by the dramatic decreases in sample weight. These reactions occur more rapidly when the ambient gas contained oxygen than when it was pure nitrogen, suggesting that oxidation reactions were also occurring.

FIGURE 5 and 6 summarize the results of mass spectrometric analysis of vapors obtained when the vapors from thermal decomposition of cellulose are introduced into the electron-impact ionizer of the mass spectrometer. The data for FIGURE 5 resulted when the sample vapor was passed through a long capillary tube on the way to the ion source of the TG-MS instrument (Mac Science). The data for FIGURE 6 were obtained with the similar instrument from Netzsch in which the sample vapor entered directly into the ion source through a conical sampling orifice or "skimmer". Thus, the sample vapor reached the EI ionizer in much less time and with much less contact with hot surfaces than when it had to pass through a long capillary tube as was the case for the data of FIGURE 5. Vapor not only condense to the cold spot of the analytical system). The most striking difference is that amplitudes of the peaks for the various species, e.g. the  $m/z$  peak of 60 due to levoglucosan, do not show a significant intensity in FIGURE 5 until the sample temperature was above 300°C. In FIGURE 6 the same peaks reached appreciable amplitudes when the sample temperature exceeded about 260°C. Clearly the rapidity with which sample vapor reaches the ionizer during "skimmer sampling" provides a less distorted representation of pyrolysis products than

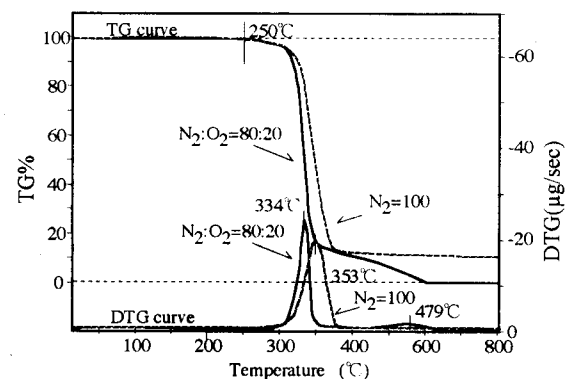


FIGURE 4. TG and DTG curves of cellulose in  $N_2$  and in  $N_2/O_2=80/20$ . Heating rate 10°C/min. Sample weight 50mg

does the much slower sampling by a long tube.

FIGURE 7 shows pyrograms obtained by Pyrolysis Gas Chromatography when the vapors from the drop type pyrolyzer were analyzed by GC-MS and pyrolysis temperatures were 300, 350 and 600°C. The peaks within the shaded area relate to levoglucosan which does not show at all at a pyrolysis temperature of 300°C (or less). It is the main species appearing at pyrolysis temperature of 350°C. At 600°C its abundance has

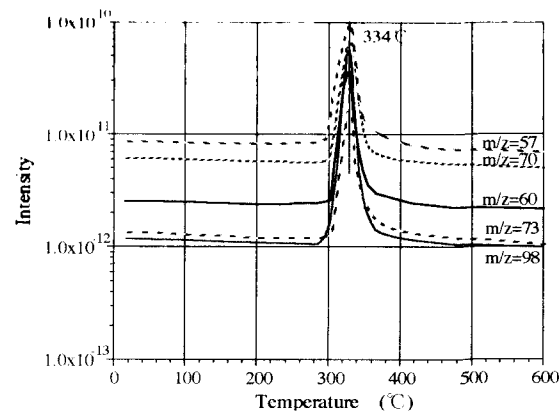


FIGURE 5. Temperature dependence of mass spectra from thermal decomposition products of cellulose. Heating rate 10°C/min. Sample weight 50mg in  $N_2/O_2=80:20$  100ml TG-DTA 2000S

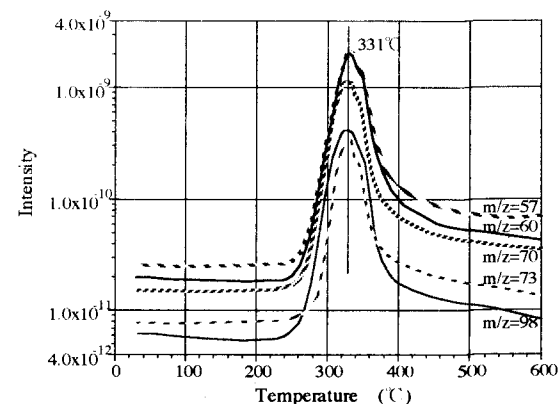


FIGURE 6. Temperature dependence of mass spectra from thermal decomposition products of cellulose. Heating rate 10°C/min. Sample weight 50mg in  $N_2/O_2=80:20$  100ml STA409C/403/5/E

decreased substantially, doubtless due to the thermal decomposition responsible for the various peaks outside the shaded area in FIGURE 7.

FIGURE 8 shows the response of the thin-film detector to the vapors resulting from increasing the temperature of a 1.6 mg sample at a rate of 10°C/min. The resistance begins to decrease at sample temperatures above 170°C. The decrease increases as temperatures rise above 250°C and reaches its maximum at a sample temperature of 350°C. When the heated sample is levoglucosan the sensor resistance begins a marked decrease at a sample temperature 170°C. This behavior strongly suggests that the species causing the resistance to decrease result from the thermal decomposition of levoglucosan. Moreover, experiments were carried out in which we measured the sensor response to vapors from each species found in cellulose decomposition products. The only such species for which an appreciable response was obtained were levoglucosan, hydroxy acetone and angelica lactone. Of these species levoglucosan is the only one with boiling point above

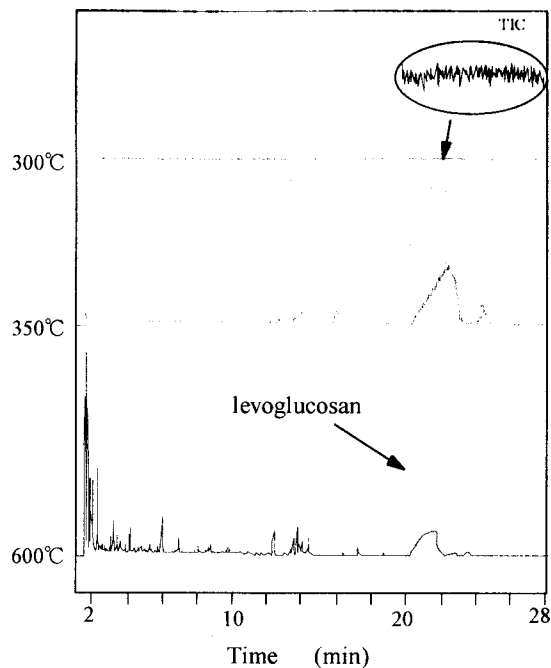


FIGURE7.  
Pyrograms of cellulose.

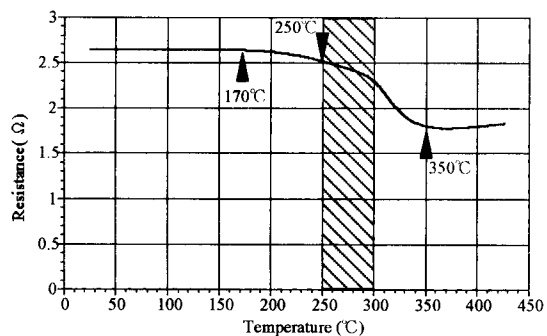


FIGURE8.  
Output of odor sensor during thermal decomposition process of cellulose.  
Heating rate 10°C/min. sample weight 1.6mg.

150°C. We conclude that the main response of the sensor during the thermal decomposition of cellulose is due to levoglucosan. In sum, the SnO<sub>2</sub> sensor shows a fairly high sensitivity but is not highly selective. Selectivity might be improved by combination with other sensors as part of a "neural network"(14).

FIGURE9 shows the dependence of amplitude on sample temperature for the mass spectral peak at an m/z value of 163 which corresponds very closely to a protonated molecule of the levoglucosan produced during thermal decomposition of cellulose. The spectra were obtained by Atmospheric Pressure Chemical Ionization (APCI) in which a corona or glow discharge produces the ions. APCI-MS grabbed the signal of levoglucosan at about 200 °C, the same temperature as human nose can detect(15).

TABLE 1 shows the results from the olfactory test of the thermal decomposition products of cellulose. By increasing temperature above 180°C, only levoglucosan shows the roasted odor and others show quite different smell.

In FIGURE 10 the resistivities

of odor sensor in various concentrations of thermal decomposition products of cellulose are measured. Data are plotted for levoglucosan hydroxyacetone α -angelicalactone furfuryl alcohol pyruvic aldehyde 5-methylfurfural diacetyl furfural and furan. These molecules are typically detected in the TG-MS analysis. Most of them have rather low boiling point of less than 170°C except angelicalactone and levoglucosan. For those chemicals, which have the high boiling point, aqueous solutions of 1.0wt% are used to produce vapors. The 1.0wt% solutions are injected in the heated pan using microsyringe. By controlling the volume of solution injected, vapor concentration in the box was controlled. For the output of odor sensor water vapor does not effect the resistivity of sensor. Odor sensor senses the vaporized chemicals. Levoglucosan showed highest sensitivity among the odor sensor outputs in the main decomposition products of cellulose.

By the combination of the results from TABLE 1, FIGURE 9 and 10, only levoglucosan has a possibility to emit roasted odors. As a result, odor sensors sensed this smell very effectively to decrease resistivity. In other words this odor sensor is the best thin film type sensor to sniff the roasted odor from thermal decomposition products before ignition.

FIGURE11 shows the sample-temperature dependence of APCI mass spectral peaks for toluene, styrene and xylene obtained during the pyrolysis of a 3mg sample of polyvinyl chloride into a stream of nitrogen flowing at 100 mL/min. The appearance of these cyclic hydrocarbons at pyrolysis temperatures as low as 60°C indicate that any fragments(10,11) of PVC packaging material that might adhere to food that is to be cooked can strongly affect its taste and in some circumstances might even have toxic effects.

In previous experiment mass spectra were obtained with Electrospray Ionization (ESI) of a solution obtained by bubbling the vapors from the thermal decomposition of a one mg sample of

levoglucosan through 50 ml of a 50-50 methanol water mixture. Mass spectrum showed a strong single peak of levoglucosan(20).

For FIGURE12 levoglucosan was heated to 350 °C by 10°C/min in the pan and residue was taken as a sample. In the process of heating up to 350°C, most of the samples might be once vaporized and condensed in the small pan. The sample was dissolved in the methanol water solution and studied by ESI-MS.

TABLE1. Olfactory test of the thermal decomposition products of cellulose.

Thermal decomposition product of cellulose	m.p.(°C)	b.p.(°C)	Roasted odor	
			less than m.p.	greater than m.p.
levoglucosan	178	281	—	○ cellulose Roasted
hydroxyacetone	-17	145		×
α -angelicalactone	18	56(b.p.12mmHg)		×
furfuryl alcohol	<RT	170		×
pyruvic aldehyde	<RT	72		×
furan	-85	31		×
5-methylfurfural	<RT	187		×
diacetyl	-2.4	88		×
furfural	-36.5	162		×

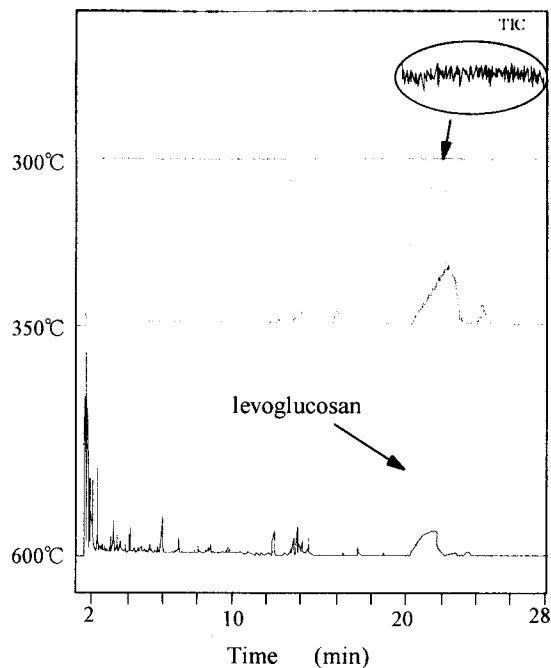


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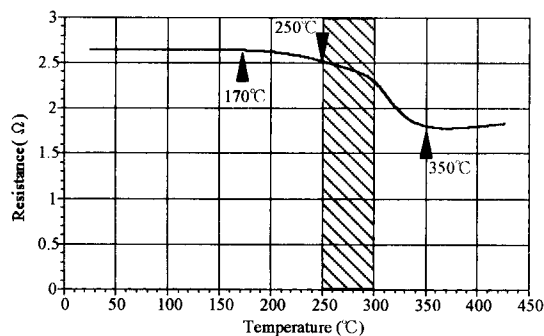


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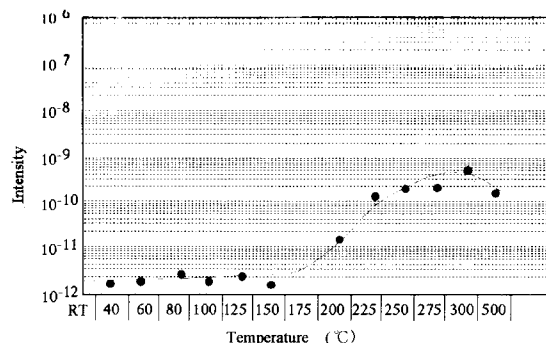


FIGURE 9. Temperature dependence of  $m/z=163$  levoglucosan peak from thermal decomposition product of cellulose. (APCI-MS)

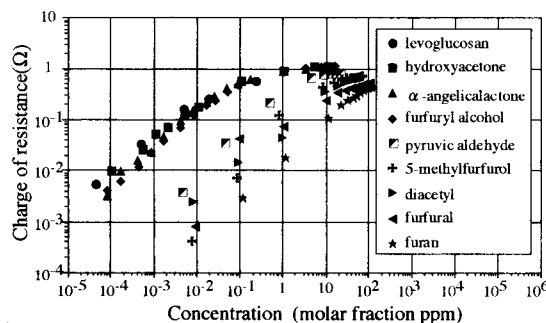


FIGURE 10. Resitivity change of odor sensor by various concentrations of thermal decomposition products of cellulose.

representative samples from different areas to a central collection point for analysis by mass spectrometry. For very large buildings the cost of mass spectrometric analysis in such a system might be economically justified. Moreover, as the cost and size of effective mass spectrometers continues to decrease the cost effectiveness of MS detection for fire prevention should continue to increase.

The interesting cluster peaks of levoglucosan are shown by this experiment. The implications of these spectrum are several: levoglucosan, a primary product of the thermal decomposition of cellulose can give rise to a variety of clusters whose electrospray mass spectra show a variety of peaks. The  $m/z$  values of those peaks provide some indication of the temperature at which their parent species were formed. Lvoglucosan could be a single-molecule only when it become very high temperature. It would thus seem possible to hope that ESI-MS analysis of vapors from the combustion of cellulose could not only serve as a signal that there is a fire but might also indicate the stage to which the fire has developed. Unfortunately, mass spectrometers are expensive and not very portable. However, one can imagine that in a large building with modern air conditioning and circulation systems it might be possible to "pipe" representa-

FIGURE 11. Temperature dependence of mass spectrum from thermal decomposition products of PVC. API-MS. Sample weight 3mg, carrier gas  $N_2$ , flow rate 100ml/min.

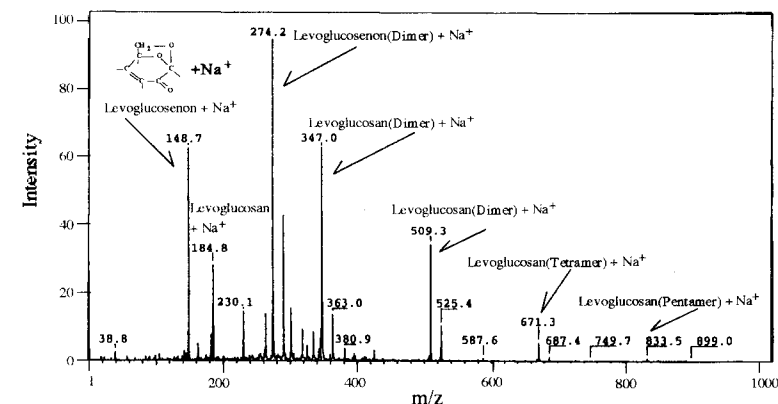
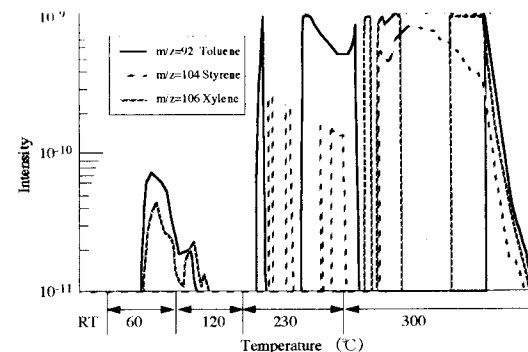


FIGURE 12. Thermal decomposition residue of levoglucosan analyzed by ESI-MS at 350°C.

## CONCLUSIONS

This potpourri of preliminary results does not pretend to provide either a recipe for effective fire detection or a design for an effective detector. It does seem to open up some new perspectives on possible routes to those objectives. The obvious next step is to obtain much more complete data on the identities of species produced in the early stages of an incipient fire as well as quantitative information on the actual detection sensitivities that can be achieved. Early detection with effective extinguishment(16) has to be pursued in order to avoid historical fire disasters(17). Recent statistical analysis showed that arson increased against accidental fire constantly. Scientific methods has been introduced to fire research in order to distinguish arson from accidental fire(18,19). We plan to pursue these important goals.

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## COMPUTATIONAL FLUID DYNAMICS