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Application of sensory-analytical techniques to odor analysis : a distillery case study.

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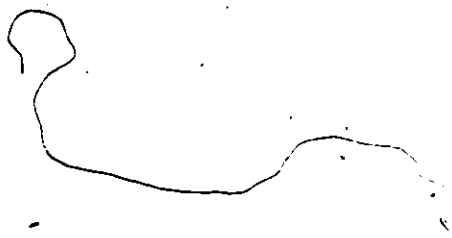

Application of Sensory-Analytical Techniques to Odor Analysis
A Distillery Case Study

A Thesis
Submitted to the Faculty of Graduate Studies
Through the Department of Chemical Engineering
in Partial Fulfilment of the Requirements for the
Degree of Master of Applied Science at the
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by

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ABSTRACT

This investigation was concerned with evaluating the relative merits of sensory-analytical techniques for elucidating the composition of odors originating from typical distillery operations.

Available literature on the theories of olfaction has been reviewed, with particular emphasis on recently proposed building block and psychophysical models. The current status of information regarding the chemical nature of odorous emissions from industrial sources is also presented.

In the experimental work, sensory-analytical techniques were used in an attempt to analyse the odorous components in spent grain syrup from a distillery operation. The laboratory procedure utilized infrared, nuclear magnetic resonance and mass spectrometers as well as a gas chromatograph equipped with a sensory splitter. The infrared and nuclear magnetic resonance spectra indicated absence of aromatic compounds. The gas chromatograph revealed that there were at least ten major odorous peaks. Their odor qualities ranged from pleasant to burnt.

The mass spectrometric results did not yield positive identification of each odorous peak, possibly due to insufficient peak resolution in the gas chromatographic column. The overall results indicate that the

syrup odor consisted of organic compounds containing sulfur, chlorine and ester groups.

Preliminary experiments were conducted on stack emissions from two different spent grain drying operations. When the results of stack gas analyses were compared to those obtained from the grain syrup, it was evident that a positive correlation existed between the two sets of observations.

ACKNOWLEDGEMENTS

The author wishes to sincerely thank Dr. G. P. Mathur, Dr. A. W. Gnyp and Dr. G. Wood for both their encouragement and continual technical advice which has made this work possible.

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I. INTRODUCTION

A sizable fraction of air quality complaints received by air management authorities concerns odors. These reactions are usually investigated by onsite testing of ambient air quality, either by human observers alone or in conjunction with dilution devices such as scentometers. Although in Canada there are, at present, no specific tolerance limits assigned to odorous pollution, the last twenty years have seen much work published that makes such limits a real possibility in the near future.

The major aims of odor investigations on industrial sources may be identified as follows.

i. to determine detectability levels of odorous emissions

ii. to determine the effectiveness of various control systems

iii. to establish the odor profiles in the neighborhood of odor discharges

iv. to analyse odorous emissions in detail by chemical and physical means to assist in meeting objectives (i), (ii) and (iii).

Of the four objectives enumerated previously, the first three have received the most attention due to the practical nature of the results obtained from investigations aimed at fulfilling these aims. The fourth objective, if it can be met, will undoubtedly remove a lot of empiricism currently necessary for describing, measuring and controlling odors. It must be admitted, however, that the present state of efforts, directed towards this goal, does not provide a great deal of optimism.

This report deals with an investigation whose objective was to attempt a fingerprinting exercise on an industrial odor. Several currently available analytical techniques were used in an effort to determine the odor composition, and in the process establish relative merits and demerits of the sensory-analytical approach to odor analysis. The work described here should be viewed in relation to similar works carried out by other researchers in the field. It is recognized that a complete analysis of most industrial odorous streams will be economically, if not technically, prohibitive. Therefore, the objective of in depth analytical investigations is to establish a firmer understanding of the place of such analysis in the overall field of odor pollution.

Although most of the engineering interest in olfaction is related to industrial odors and their control, smell, as one of the primary human senses, has much basic

interest in its own right. Over the past forty years, many scientific works have attempted to explain the mechanism of olfaction. Of somewhat more practical interest than the mechanistic studies are the so called theories of olfaction which are discussed in Chapter II, where major emphasis is placed on two recent olfaction models.

The primary engineering interest in analytical odor research is in determining which and what types of compounds are present in the odorous streams. Chapter III summarizes the present knowledge regarding odorous emissions from different industrial operations. This chapter also reviews odor problems associated with grain drying operations, an area of special concern during this investigation.

A combination of sensory and analytical methods is generally used to determine the nature of the compounds in an odorous stream. A synopsis of various sensory-analytical methods in current use is presented in Chapter IV. A particular application of these methods was the essential subject matter of this present work. The results of analyses using infrared, nuclear magnetic resonance, gas chromatography and mass spectroscopy are presented in Chapter V.

Chapter VI provides a discussion of the results and some conclusions regarding the overall merits of sensory-analytical methods in odor research.

II. THEORIES OF OLFACTION

Among the known senses of man, olfaction has been the most neglected. As a result, very little is known about the mechanism of olfaction. There is some agreement regarding requirements that any material must meet in order to be clearly odorous. It is generally accepted, for example, that an odorous material must have lipid solubility as well as water solubility, although the latter can be very low. It must also have sufficient volatility, and must be present in the air surrounding the receptor site at some minimum level (threshold concentration). The threshold concentrations can vary enormously for different odorants.

Along with the above requirements, it is an accepted fact that there must be a physical contact between the odorant molecules and the receptor sites in order for the odor to be perceived. Most researchers in this field also agree that the odorant-receptor interaction is a physical rather than a chemical process. In other words, the odorant does not have to undergo a chemical conversion in order to be perceived.

Beyond the above agreements there is a great diversity of opinion regarding the actual mechanism of olfaction. Some people believe that there is no general relationship between odor and chemical structure because there are as

many different odors as there are odorous chemical structures. Nonetheless, a number of theories of olfaction have been postulated. The state of the art has been reviewed, among others, by Dravnieks [1] and Klopping [2]. Four of the many existing theoretical viewpoints are discussed below.

A. Henning Olfactory Model

One of the earlier olfactory models was that proposed by Henning. This model has been discussed in a number of references [3, 4]. The model consists of a triangular prism with 6 'fundamental' or 'primary' odors located at the corners of the prism as shown in Figure 2.1. All other smells were considered mixtures of these six primary odors and were located on the edges and surfaces of the prism. Thus, odors consisting of two primary ones would be placed along the edges of the prism. The triangular surfaces would be occupied by the odors consisting of three primaries and the square surfaces by those consisting of four primary odors. Henning attempted to associate each of the six primary odors with the chemical constitution of the molecules. For example, he said that the flowery primary was due to the ortho (1:2) arrangement of functional groups on a benzene ring. Spicy smells were associated with a para (1:4) arrangement. Thus Henning concluded that any odorant showing both flowery and spicy sensation would have both ortho and para groups and would be placed on the flowery-spicy edge of the prism.

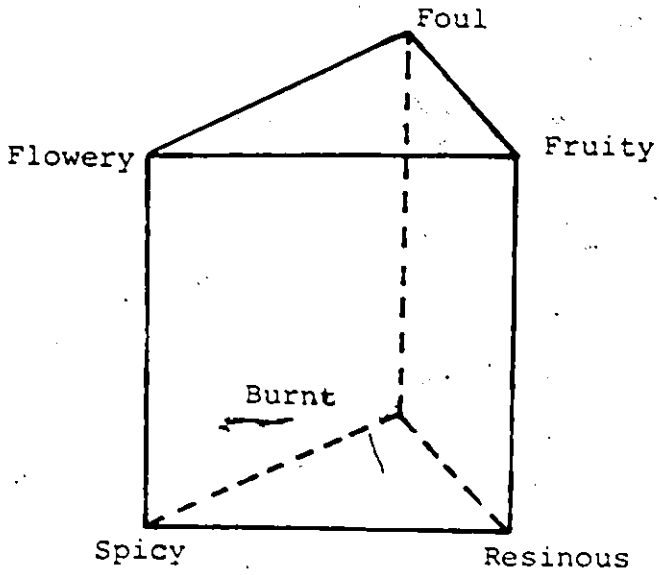


FIGURE 2.1: Triangular Prism Proposed by Henning as an Olfactory Model

Henning's model has several shortcomings. One of the major ones is that it is not possible to place an odorous mixture such as foul-fruity-burnt in the prism, because it is placed on the rectangular surface. To place it on that surface, a resinous description must also be given.

B. Dyson-Wright Vibrational Theory

In 1937-38 Dyson [5] suggested that in order for a compound to be odorous, it must have volatility, lipid solubility and intermolecular vibrations which give rise to Raman shifts in the region 1400-3500 cm^{-1}. This theory was not taken seriously because of a demonstrated lack of

correlation between odors and the suggested frequency range. Twenty years later, Wright [6] found that the olfactory receptors are in fact sensitive to a certain range of vibrational frequencies but that the frequency range suggested by Dyson was wrong. He proposed a vibrational range of 50-700 cm^{-1}, which is in the far infrared region.

In Wright's theory, the quality of an odor is determined by the vibrational frequency, while the strength of the odor depends on volatility, adsorptivity and water-lipid solubility.

There are two deficiencies in the Dyson-Wright theory of olfaction. One of them is that isotropic molecules have the same odor but different vibrational frequencies. Examples of this are H_2S and D_2S, CH_3CHO and CD_3CHO. The other drawback is that some optical isomers exhibit the same vibrational frequencies, but only one isomer is odorous.

The vibrational theory cannot account for the powerful odors of certain small molecules such as H_2S, NH_3 and HCN, which possess no low frequencies.

C. Moncrieff-Amoore Stereo Chemical Theory

Moncrieff [7] proposed a theory of olfaction in which he stated that the only prerequisites for odor were

volatility and suitable solubility. A later modification [8] postulated that the two prerequisites were volatility and a molecular configuration complementary to the sites of the receptors.

Amoore [9, 10] extended Moncrieff's theory by determining how many types of receptor sites existed. He also analyzed the size and shape of the receptor sites through an extensive survey of the literature on compounds with recorded odors. By grouping the compounds according to their characteristic odors and then studying the corresponding molecular structures, he concluded that, among the rigid molecules, the most common odor description indicates the identity of the corresponding primary odor (i.e. odor perceived when only one type of receptor site is stimulated). Amoore found that there were 14 groups into which odors could be classified. Seven of the most frequently occurring groups were considered to be primary odors. Table 2.1 gives the frequency of occurrence of different types of odors.

The shape and size of receptor sites for each of the primary odors were established from a study of the shapes and sizes of the molecules which had that primary odor. This stereochemical description of odors implies that each primary odor originates from molecules that have similar shape and size.

	Odor	No. of Compounds
1.	Camphoraceous	106
2.	Pungent	95
3.	Etheral	53
4.	Floral	71
5.	Pepperminty	77
6.	Musky	69
7.	Putrid	49
8.	Almond	30
9.	Aromatic	27
10.	Aniseed	12
11.	Lemon	7
12.	Cedar	7
13.	Garlic	7
14.	Rancid	6
		616

TABLE 2.1: Frequency of Occurrence of Different Types of Odors [10]

Figure 2.2 shows the proposed human olfactory receptor sites corresponding to the seven primary odors together with molecules representative of each odor. In this illustration, all the sites are shown in perspective, from above and side, with dimensions given in Angstrom units.

The basic postulation of the stereochemical theory is that molecular models of compounds should correspond to the odor characteristics as per Figure 2.2. Amoore demonstrates excellent size and shape fit for more than seventy substances. The stereochemical theory has also been used

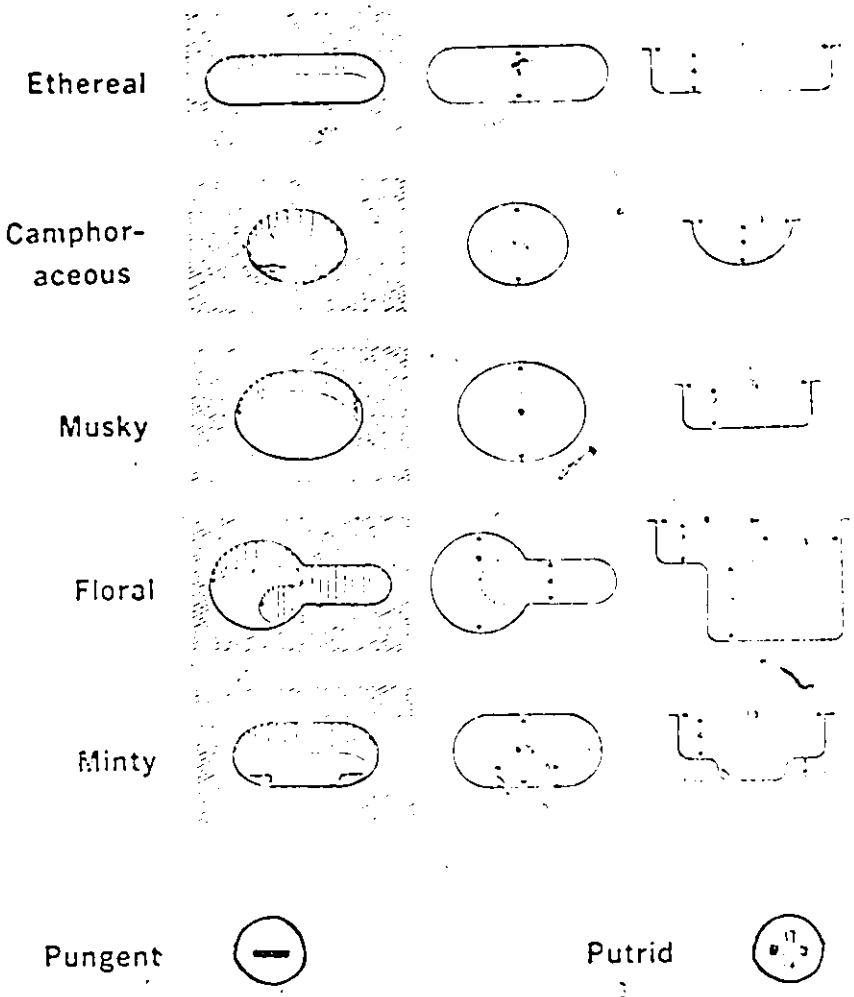
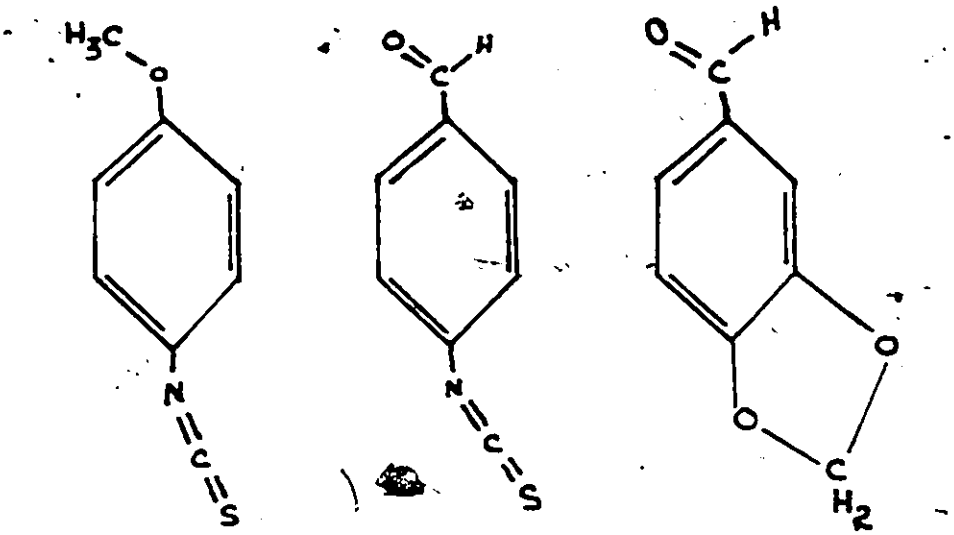


FIGURE 2.2: The Human Olfactory Receptor Sites Corresponding to the Seven Primary Odors [9]

with some success in predicting odor qualities for newly synthesized substances, and for tailoring a specific odor by mixing up primary odors. The stereochemical theory, like the vibrational theory, is unable to explain odors of small molecules.

D. The Profile-Functional Group (PFG) Concept

In 1957, Beets [11] postulated that the odor of a molecule is determined by two separate contributions; one from the form and bulk of the molecule and the other from its functional group or groups. Beets found that the odor quality is more dependent upon the position of the functional group than upon its nature. For example, upon comparing the odors of substituted phenylisothiocyanates he found that the odor quality was far more dependent upon the position of substitution than upon the nature of the group. He noted that the para position always corresponded to the ethereal odor and the ortho and meta positions to pungent odors irrespective of whether the group was acetyl, methoxy (I) or ethoxy. Beets also found that if an aldehyde group is introduced into the para position (II), an odor similar to heliotropine (III) is obtained.



I II III

Based upon his research, Beets concluded that the odor of a molecule is determined by the dominant functional group. In (I), -NCS group dominates and in (II) the aldehyde group dominates.

Theoretically, the Profile Group Concept is acceptable to an extent, but it will still take considerable experimental work to find which group in a given compound is dominating.

E. Recent Advances in Olfaction

There is no accurate model available that can predict the olfactory quality of a substance from its physiochemical properties. Many attempts have been made to relate odor quality to the physical and chemical properties of molecules, but each of them explains only part of the puzzle.

In recent years, more elaborate efforts to establish odor correlations or models have been made.

1. Building Block Models

Dravnieks [12] conducted a study to determine if simple paperplane structural formulae, useful as a shorthand for chemical deductions, could also contain sufficient information for positive correlation with the principal odor properties. Since the process is based on an enumeration of the structural elements of the molecules, models based on this approach may be regarded as building block models.

The psychophysical properties studied by Dravnieks were

i. odor threshold

ii. psychophysical intensity functions that describe the change in odor intensity with the odorant concentration

iii. odor quality

iv. structural features

a. Odor Threshold

Odor threshold is the concentration at which the odor of a substance is just detectable by the human nose. To determine odor thresholds, Dravnieks [12], used a triangular port technique. At each odorant concentration, two room air stimuli and one odorant stimulus were supplied to three adjacent ports. Each panelist was asked to select the stimulus having an odor different from the other two. The procedure was repeated for each dilution level, always proceeding from low to high odorant concentrations. Dravnieks assumed consistent detection at three consecutive concentration levels of odor to be an indication that detection began at the lowest of these three levels. The panel observations were converted to $E.D._{50}$ values, called Effective Dosage at fifty percent level, by a procedure evolved earlier by Dravnieks and coworkers. This number represents the dilution level at which an odor will begin to be detected by 50% of the panel.

b. Psychophysical Intensity Function

Various dilutions of the vapor of an odorant were matched against their odor intensities on an odor scale based on 1-butanol. The panelists were asked to ignore the odor-character differences between the test substance and 1-butanol, but to indicate at which point the intensities matched. Typical plots of the logarithm of the odorant vapor dilution vs the logarithm of the matching 1-butanol concentration are shown in Figure 2.3. From Figure 2.3 it can be seen that the psychophysical function with reference to 1-butanol can be written as

$$\text{odor intensity} = k\,(\text{concentration})^{n}$$

Dravnieks [12] suggested that, since the psychophysical intensity of 1-butanol changes proportionally to the 0.63 power of its concentration, the slopes in Figure 2.3 multiplied by 0.63 would give the true value of the psychophysical exponent, n.

c. Odor Quality

In tests for odor quality the odorants were rated on their odor similarity with respect to one another on a 0-7 scale (0 = no similarity; 7 = same odor).

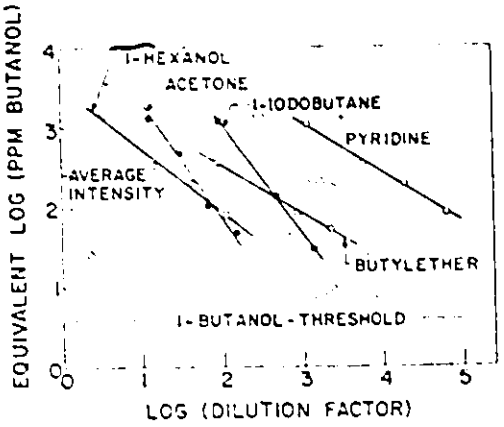


FIGURE 2.3: Change of Odor Intensity with Dilution of Odorant Vapor [12]

d. Structural Features of Odorant Molecules

For each of the odorants the following features were enumerated:

i. number of atoms in the molecule, which is approximately indicative of the size of the molecule

ii. longest dimension within the molecule, in terms of the number of atoms, indicative of the length of the molecule

iii. number of features generating bulkiness

iv. number of multiple bonds between carbon atoms

v. number of sulfur atoms, except those connected to oxygen

vi. number of nitrogen atoms, except those connected to oxygen

vii. number of halogen atoms

viii. presence of -OH group

ix. presence of -COOH group

x. presence of ester group

xi. presence of ether group

xii. molar refractive increment of each of those three bonds that exhibit the longest increments (largest electronic polarizability)

xiii. position of the most polarizable bond in the molecule

xiv. distance, in the terms of the number of atoms, between the most polarizable and the next most polarizable bond.

A statistical analysis was performed by Dravnieks in an effort to find possible correlations between the odor properties and the previously listed structural features of the odorant. The equation used was of the form

$$Y = A_o + A_1 F_1 + A_2 F_2 + \cdots A_i F_i + A_1^2 F_1^2 + A_2^2 F_2^2 + \cdots A_i^2 F_i^2 + A_{12} F_1 F_2 + \cdots A_{ij} F_i F_j + A_{12}^2 F_1^2 F_2 \cdots + A_{ij}^2 F_i^2 F_j \qquad 2.2$$

where F represents a feature.

In Equation 2.2 the terms A_i test for simple significance of the respective features. The terms A_i^2 contains the square of the magnitude of the feature i, and test if the odor significance of feature i may have a minimum, or a maximum, or increase more than proportionately with the magnitude of feature i. The A_{ij} terms postulate that feature i has a different effect at different magnitudes of feature j or vice versa. The A_{ij}^2 term postulates that feature j have a maximum effect, or a minimum effect, at a certain value of feature i.

Dravnieks [12] reported values of ED_{50}, Z and n for the 33 odorants shown in Table 2.2. The magnitude of Z establishes the dilution necessary to obtain an odor intensity equivalent to that of 250 ppm of 1-butanol in air.

Dravnieks subjected his own and five other sets of data to a multiple regression analysis. Table 2.3 lists the results of the sequential multiple regression analysis of the threshold data. Because the maximum number of independent terms was limited to four, a restriction was imposed on the use of some of the more specific molecular features that could occur in only one or a few of the odorants. This abbreviated statistical treatment indicated that

	Odorant	Dilution to E.D.$_{50}$	Log E.D.$_{50}$	Log Z	Slope n vs. 1-butanol*
1	Acetone	400	2.60	1.87	1.38
2	Acetonitrile	100	2.00	1.32	1.24
3	Benzene	800	2.90	2.01	1.20
4	2-Butanone	1500	3.18	2.38	1.20
5	Butyl ethanoate	26500	4.42	2.54	0.67
6	Butyl ether	6300	3.80	2.53	0.58
7	Carbon tetrachloride	220	2.34	1.21	1.10
8	Chloroform	820	2.91	1.87	1.07
9	Cyclohexane	140	2.15	1.32	1.23
10	1,2-Dichloroethane			1.63	0.83
11	2,4-Dimethylpentane	170	2.22	0.97	1.06
12	1,4-Dioxane	700	2.85	1.78	1.77
13	Ethanol	100	2.00	0.55	1.19
14	1-Hexanal			3.12	0.98
15	1-Hexanol	18300	4.26	1.77	0.80
16	2-Hexanol		2.46		
17	1-Iodobutane	2770	3.44	2.66	1.25
18	Mesitylene	1580	2.76	1.49	0.79
19	2-Methyl-2-propanol	50	1.68	1.01	1.03
20	Nitropropane	90	1.95	1.51	1.33
21	1-Octene	21000	4.32	2.48	0.68
22	2-Octene	17900	4.25	2.72	0.84
23	2-Octyne	29700	4.47	3.60	0.74
24	3-Pentanone	25300	4.40	3.13	1.09
25	1-Propanol	660	2.82	1.17	1.00
26	2-Propanol	90	1.96	1.27	1.11
27	2-Propenol	15200	4.18	2.97	1.14
28	Propylbutanoate			2.53	0.75
29	Pyridine	14200	4.15	3.29	0.94
30	Styrene	4900	3.69	2.32	0.88
31	1,1,2,2-Tetrachloroethane	1130	3.05	2.27	0.99
32	Thiophene			4.04	0.62
33	Toluene	2150	3.33	2.23	0.98

*n Multiplied by 0.63 gives the exponent n for the function (odor intensity) = kC^n where C is the odorant concentration.

TABLE 2.2: Experimental Data on Parameters Related to Odor Intensity [12]

	Author	Number of Odorants	Medium	Units: log of	F-Ratio	Probability Chance	Coefficient of Determination
1.	Dravnieks and Laffort	29	air	dilution from saturation	8.3	<0.001	0.58
2.	Katz-Talbert	52	air	ppm(vol)	10.4	<0.001	0.47
3.	Leonardos et al	50	air	ppm(vol)	7.2	<0.001	0.39
4.	Laffort	64	air	µg/l	10.8	<0.001	0.42
5.	Evans et al	36	oil	ppm(wt)	16.5	<0.001	0.68
6.	Salo	43	water + alcohol	mg/l	10.3	<0.001	0.52

TABLE 2.3: Regression Analysis Study of Odor Threshold Data: Four Variable Terms [12]

for all six sets of data there was a significant correlation between the threshold values and the structural features. Inspection of the structural features selected by the sequential regression process suggested that the important terms were not independent features but the crossterms representing interaction. For example the total number of atoms frequently appeared either as a product of this number and the highest (one or more) bond polarizabilities, or as a product with the presence of -OH group, or with the number of multiple bonds, or with the number of S or N atoms.

Dravnieks also correlated log (Z), values of which are shown in Table 2.2, to the structural features using a regression equation with five variables. Because the log (Z) correlation was somewhat better than the threshold correlation he concluded that it might serve as a better positioning point for predicting the log (intensity) vs log (dilution) plots shown in Figure 2.3.

When Dravnieks analyzed the odorants listed in Table 2.2 using a five term regression equation he found that a significant correlation existed between the exponent of the psychophysical intensity function and the structural features. Figures 2.4 and 2.5 show the goodness of fit for correlations of ED_{50} and log (Z) values for the Dravnieks data [12].

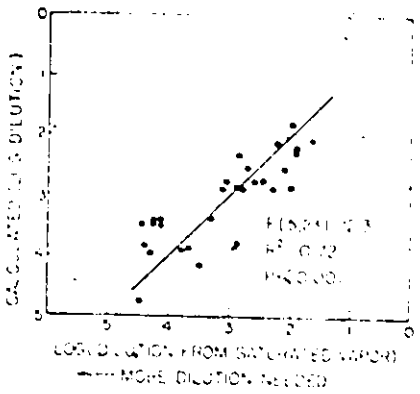


FIGURE 2.4: Comparison of Experimental Values of Dravnieks to Calculated $E.D._{50}$ Values from Regression Equation [12]

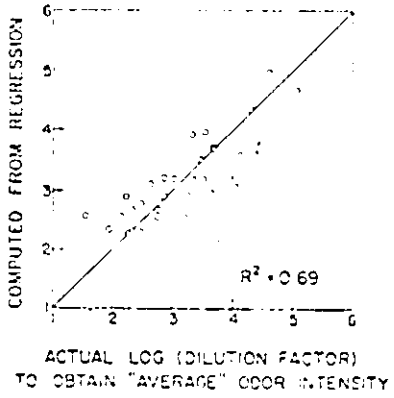


FIGURE 2.5: Comparison of Experimental Values of Dravnieks to Calculated Values of Odor Intensity, Equivalent to that of 250 ppm of 1-butanol in Air Obtained Using the Regression Equation [12]

Dravnieks acknowledges that the building block models, of the type he investigated, will have to be refined considerably before generalized conclusions regarding the significance of different features can be formulated.

In a more recent paper, Dravnieks [13] has extended correlations between odor intensities and structural properties of odorants. Using a butanol reference scale for measuring intensities he correlated them to thirty-eight attributes derived from an inspection of Wiswesser notations which utilize symbols for certain structural characteristics of molecules (e.g. U for double bond, R for benzene ring). He concluded that this approach has promise, although the correlations obtained so far show considerable scatter.

2. Psychophysical Models

Schiffman [14, 15] has put forward a model based on a psychophysical approach to the determination of the physiochemical dimensions of odor. She used a quantitative approach relating psychophysical measures with physiochemical values to compare her findings with the theories put forward by Henning, Amoore and Wright. A multidimensional scaling method provided the relationship between the psychological dimension

of olfaction and the physiochemical variables. This multidimensional scaling can place the results of experimentally determined olfactory sensations from certain odors so as to reveal relationships and distances among the olfactory stimuli. In principle, if two substances are found to have a similar quality, they will be placed near each other in a multidimensional quality space, whereas substances judged not similar will be located far away from each other. To generate a multidimensional quality space, she used the data of Wright and Michels [16] and Woskow [17]. The resulting spaces from these two data sets are shown in Figures 2.6 and 2.7. These two spaces are considered rather similar in that they both contain distinguishable groups of pleasant (left of Figures 2.6 and 2.7) and unpleasant odors (right of Figures 2.6 and 2.7). Further analysis of Wright and Michels data was carried out to break up each group into its own two dimensional spaces. These spaces are shown in Figures 2.8 and 2.9. These two figures were used by Schiffman to investigate possible odor relationships to psychological variables such as odor quality and to physicochemical variables such as molecular structure, functional groups, molecular weight and Raman spectra.

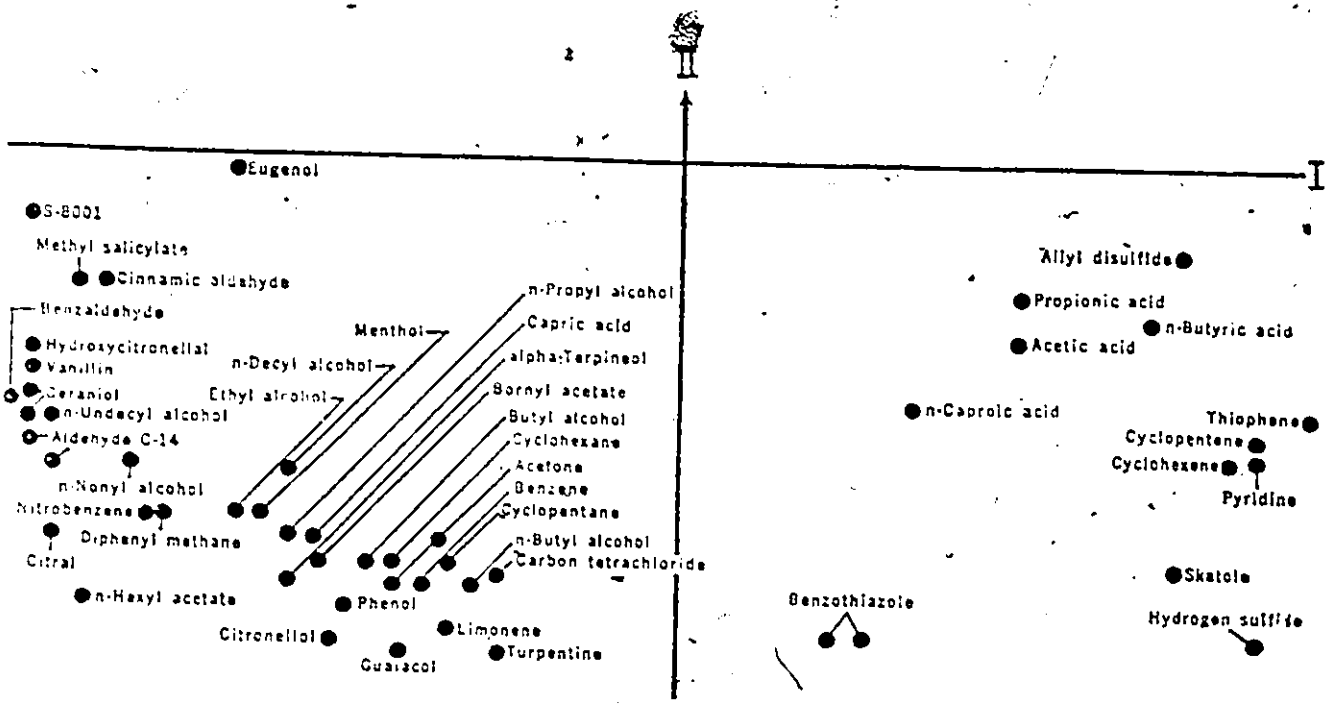


FIGURE 2.6: Two-Dimensional Solution of Wright and Michels' Data Using Guttman's Method as Obtained by Schiffman [14]

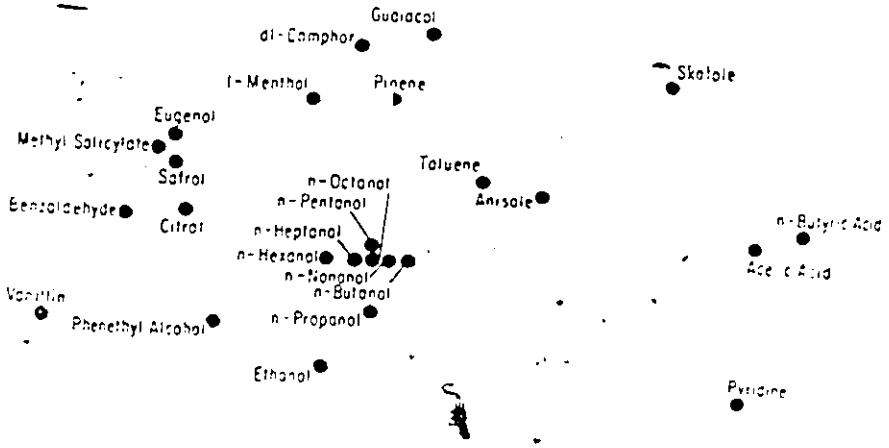


FIGURE 2.7: Two-Dimensional Solution of Moskow's Data Using Guttman's Method as Obtained by Schiffman [14]

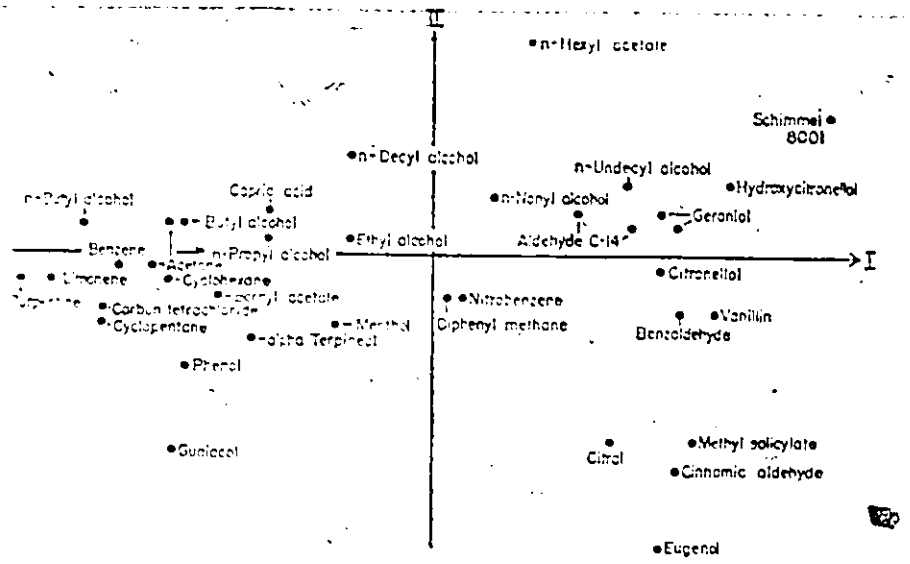


FIGURE 2 8: Two-Dimensional Solution of the Pleasant Stimuli in Figure 2.6 [14]

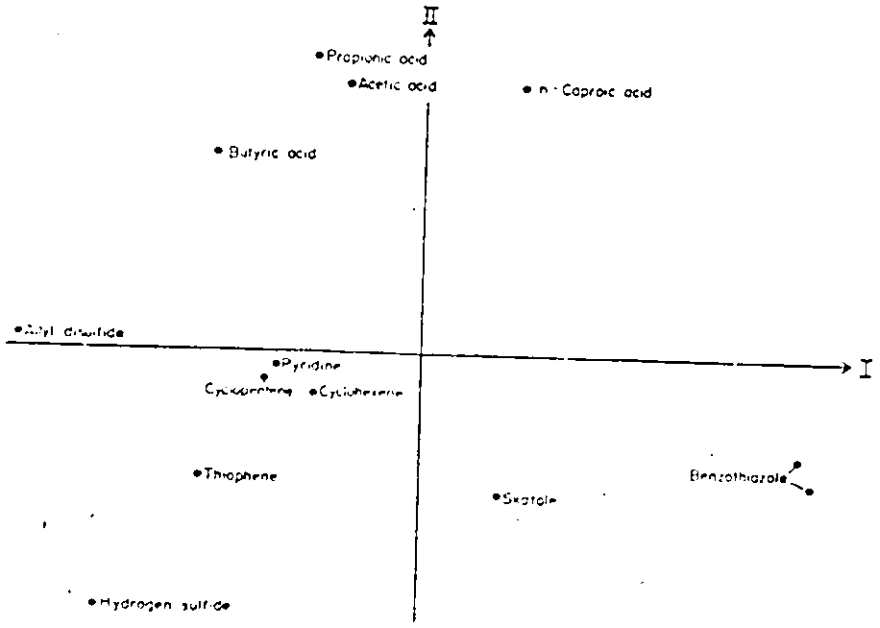


FIGURE 2.9: Two-Dimensional Solution of the Unpleasant Stimuli in Figure 2.6 [14]

a. Odor Quality

In going from right to left in Figure 2.8, the odor quality changes from flowery, pleasant to more spiritous and resinous. In going from top to bottom, there is a general increase in sharpness of odor. These trends are shown in Figure 2.10. For the unpleasant odors, no odor quality trends are obvious from Figure 2.11.

b. Molecular Structure

When Schiffman examined the molecular structure dependence of stimuli shown in Figures 2.8 and 2.9, she found a slight trend, especially for cyclic molecules, but it was impossible to conclude whether stereochemical properties alone can determine the olfactory quality of a compound. This observation seems in contradiction to Moncrieff-Amoore stereochemical theory discussed earlier in this chapter.

c. Functional Groups

After examining Figures 2.12 and 2.13, which are the functional group representations of Figures 2.8 and 2.9, Schiffman concluded that the functional groups seemed to be good distinguishing parameters for odor quality. She found that aldehydes, esters, alcohols, phenols, ketones and ethers

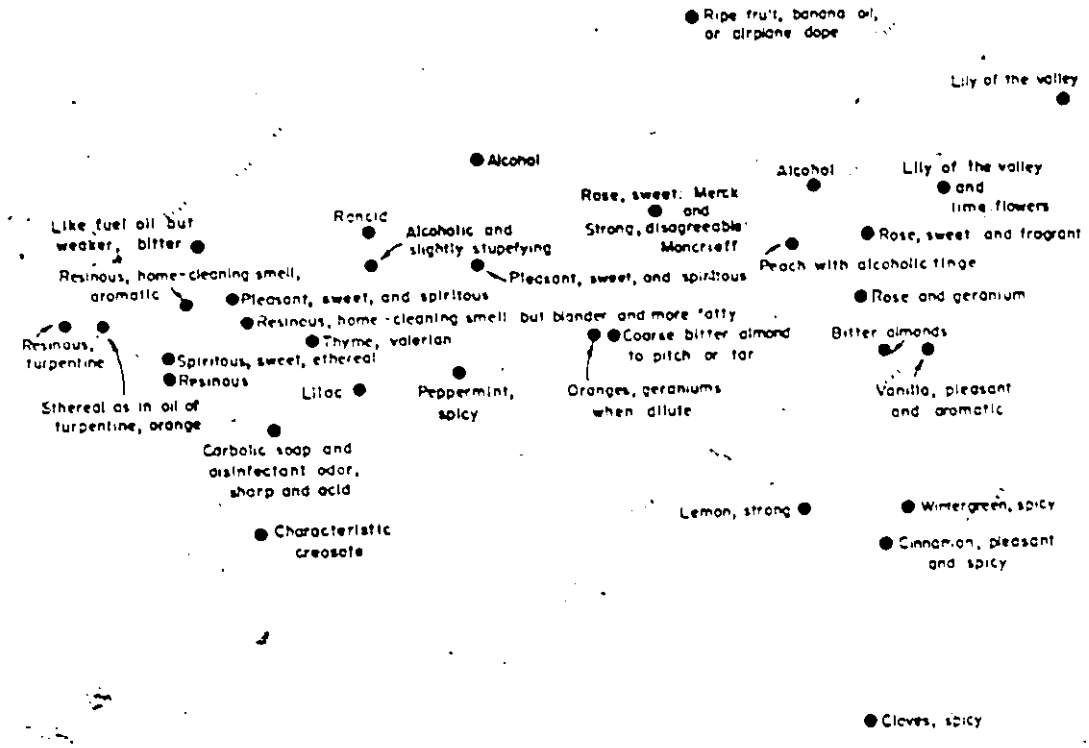


FIGURE 2.10: The Olfactory Qualities Associated with the Pleasant Stimuli in Figure 2.8 [15]

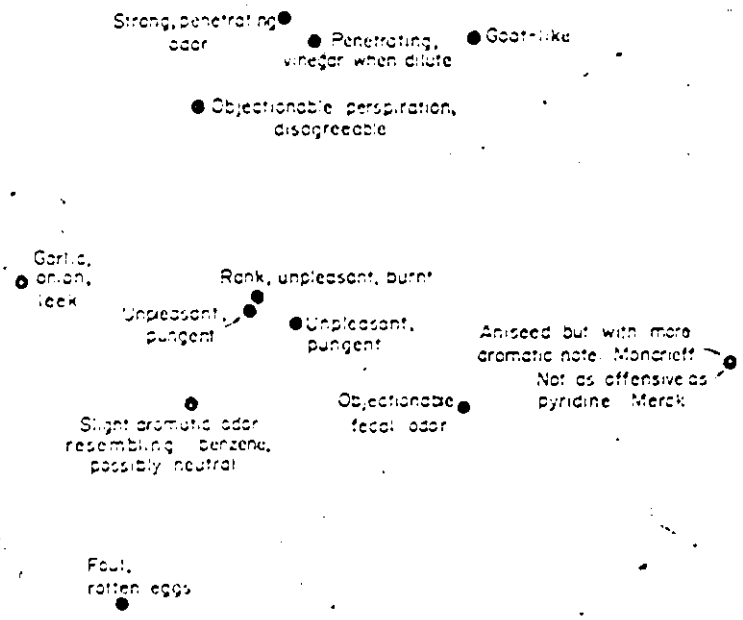


FIGURE 2.11: The Olfactory Qualities Associated with the Unpleasant Stimuli in Figure 2.9 [15]

FIGURE 2.12: Functional Group Associated With the Pleasant Stimuli in Figure 2.8 [15]

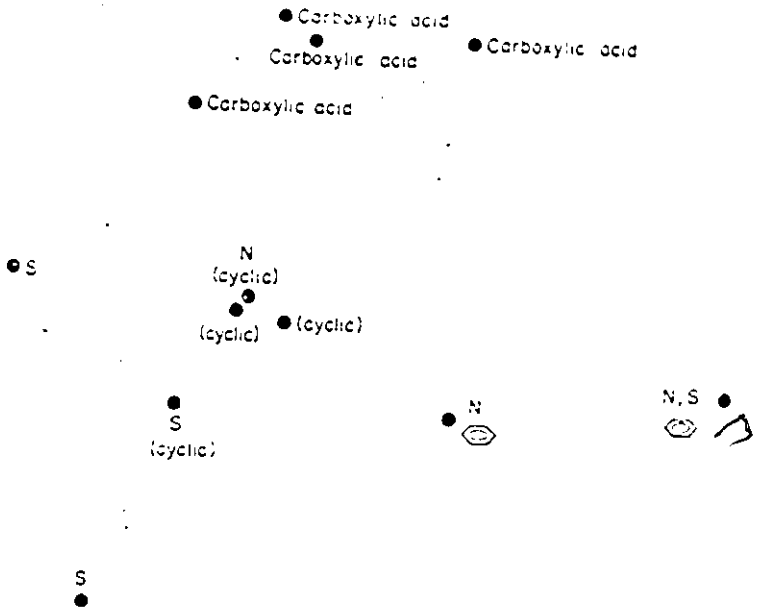


FIGURE 2.13: Functional Group Associated With the Unpleasant Stimuli in Figure 2.9 [15]

all fell into the pleasant area of the space whereas the sulfur and nitrogen containing compounds, as well as light carboxylic acids, were located in the unpleasant region. In addition, the functional groups tended to cluster together. For example, in Figure 2.12, the aldehydes all appear in the upper right hand part of the schematic representation.

d. Molecular Weights and Boiling Points

Schiffman also examined the molecular weights and boiling points of the stimuli shown in Figures 2.8 and 2.9. Because boiling points and molecular weights are highly correlated, she concentrated on the molecular weights. This approach indicated that there were general trends. For example, the more flowery, fruity odors tended to have higher molecular weights while molecular weights for odorants in the unpleasant space were generally lower than those for the more acceptable odors.

e. Raman Spectra

An examination of the Raman spectra of the molecules depicted in Figures 2.8 and 2.9 showed that the vibrational frequencies in the 100 to 1000 cm^{-1} range contained information only about the "goodness" or "badness" of one odor, but could not differentiate the quality any further. In

general, there was no particular trend relating quality to the number of double bonds, dipole moments, water solubility or freezing points.

Schiffman and coworkers [14, 15] have been working on a weighting scheme which, when applied to the physicochemical variables, could perhaps generate the kinds of spaces shown in Figures 2.6 and 2.7. These researchers have achieved partial success in their efforts.

Although the Schiffman technique of multidimensional scaling has been questioned by some researchers [18], it does appear to be a potentially useful means of deciphering the fundamental dimensions responsible for the sensation of odor.

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III. ODOROUS EMISSIONS FROM INDUSTRIAL OPERATIONS

The following general survey of industrial odor pollution provides an introduction to the emission problems associated with the grain drying operations at the Hiram Walker and Sons' Limited plant in Walkerville, Ontario. The major portion of the experimental phase of this investigation was concerned with the identification of compounds responsible for the odors generated during the reclamation of spent grain in a flash drying system.

A. General Classification

Due to the complex nature of most industrial effluents very little is usually known about the composition of odorant streams. For different industries, general classes of chemicals have been identified as being associated with odorous effluents as shown in Table 3.1. A good review of emissions, according to industry type, has been presented by Haring, Okey and Turk [1]. The following discussion is adapted from this reference.

1. Pulp and Paper Industry

This industry is a major source of odor pollutants. Sodium sulfide, which is a major component in the alkaline liquor, generates a numbor of odorants, including hydrogen sulfide, mercaptans, sulfides and disulfides.

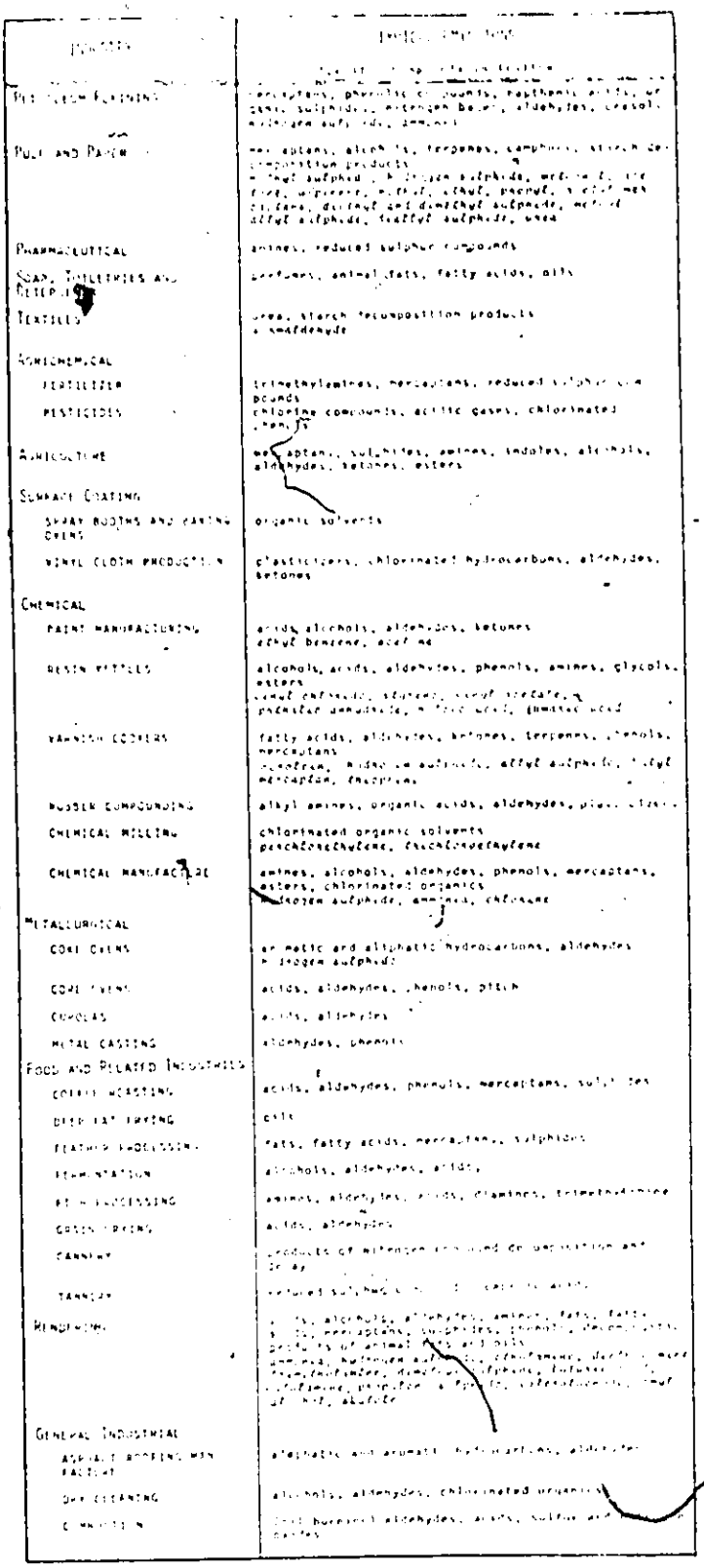

TABLE 3.1: Industrial Odorous Emissions [2]

2. Petroleum Industry

This is another major source of odor pollution. The emissions vary from refinery to refinery, depending upon the operations involved. The most common odorants are mercaptans, organic sulfur compounds, ammonia, hydrogen sulfide and sulfur dioxide.

3. Phthalic Anhydride Production

During the production of phthalic anhydride from naphthalene or o-xylene, naphthaquinone, maleic and benzoic acids, cyclohexanes and many other odorous compounds are evolved.

4. Fertilizer Industry

In the fertilizer industry the major sources of odorants are nitrogen oxides from nitric acid, ammonia, urea and formaldehyde, as well as fluorides.

5. Resin Manufacture

Most resins, particularly vinyl polymers and copolymers, require plasticizers to improve their workability. Finished plastics are made with heated mixtures of resins, fillers and plasticizers. During these processes, odorous vapors and mists are given off.

6. Rubber Processing

Because raw rubber is too soft for most commercial uses, it must be cured to reduce its plasticity. Many of these additives used in the curing have substantial vapor pressures. When the rubber is treated odorous exhaust gases are released. The common odorants are alkyl amines, aldehydes, organic acids and plasticizers.

7. Adhesive Manufacture

The three common types of adhesives are protein, starch and synthetic resins. The protein adhesives include many fish and animal by-products that are degreased with petroleum naptha, hydrolyzed by lime treatment and dried. During these processes odorous nitrogen and sulfur compounds are emitted.

8. Pesticide Production

There are so many different pesticides that it is difficult to generalize the types of odors emitted from the various plants. For example, during the manufacture of DDT, vapors of alcohol, chlorine, chloral, chlorobenzene, sulfur dioxide and hydrochloric acid are emitted. The manufacture

of the herbicide 2, 4-D is responsible for vapors of alcohols, chlorine, chlorol, chlorobenzene, sulfur dioxide, hydrochloric acid, phenol, chloroacetic acid, dichlorophenol and many other odorous compounds.

9. Pharmaceutical Preparation

Although pharmaceuticals comprise a long list of synthetic compounds, two types of naturally occurring operations create especially difficult odor problems. Fermentation is responsible for emissions of gases produced during the process itself or as a result of treatment of waste products such as spent mashes and micellae. Biological production schemes are also potential odor sources. One example of odor generation is during the treatment of beef hung to produce a blood anticoagulant.

10. Essential Oil Formulation

Essential oils are natural or synthetic chemicals used for perfumes and for flavoring foods. Their odors are normally pleasant, but when present in high concentrations near the manufacturing plant they can become obnoxious.

11. Textile Industry

The textile industry converts natural fibers and synthetic organic polymers into finished materials. Most of the odor problems arise during the spinning operations of synthetic polymers. They are generally due to the solvents. During fiberglass spinning, phenolic and spent phenolic odors are also produced.

12. Food and Agricultural Operations

The food and agricultural industries are sources of a wide variety of odors. In animal husbandry, the major odorants are ammonia, hydrogen sulfide, aliphatic alcohols, aldehydes, various organic amines, mercaptans and sulfides. In fermentation processes, the odor is due to drying of spent grain, loss of alcohol in the fermenters, stills and during storing.

13. Tanneries

Tannery odors reflect the proteinaceous nature of hides, hair and flesh. The most common odor components are acids, alcohols, aldehydes, ammonia, hydrogensulfides, mercaptans, sulfides and phenols.

14. Municipal Waste Treatment

Municipal waste treatment plants emit many organic gases including mercaptans, sulfides, ammonia and hydrogen sulfide.

B. Odor Problems of Grain Drying Operations

Most of the grain processing industries utilize only the starch content of the grain. The remainder, known as spent grain, contains almost all of the proteins, fats, minerals, vitamins and fibers of the original cereal [3]. This spent grain is an important factor in the profitability of several food processing industries since it can be sold as feed for chickens, swine and cattle. In earlier times, fresh spent grain was fed directly to local farm animals, but as the grain processing industries expanded the increasing amounts of spent grain could not be used in the immediate areas. As a result sophisticated drying operations were needed before the grain could be shipped to outlying regions.

According to First and coworkers' [3] analysis of the distilling industry, de-alcoholized fermentation residues are generally discharged from beer stills as a mash containing about 7% solids. This material is screened and pressed to form a cake containing about 17% solids before charging to the dryer. In addition, about 80% of the dried material, containing 90% solids, is recycled through the dryer to produce a combined feed stock containing up to 60% solids. This mixing of dry and wet products provides the additional bulk needed for proper performance of the dryer. Figure 3.1 shows a schematic representation of a typical spent grain recovery system in a distillery. Normal operation conditions and mass balances for each step of the process are also provided by this illustration.

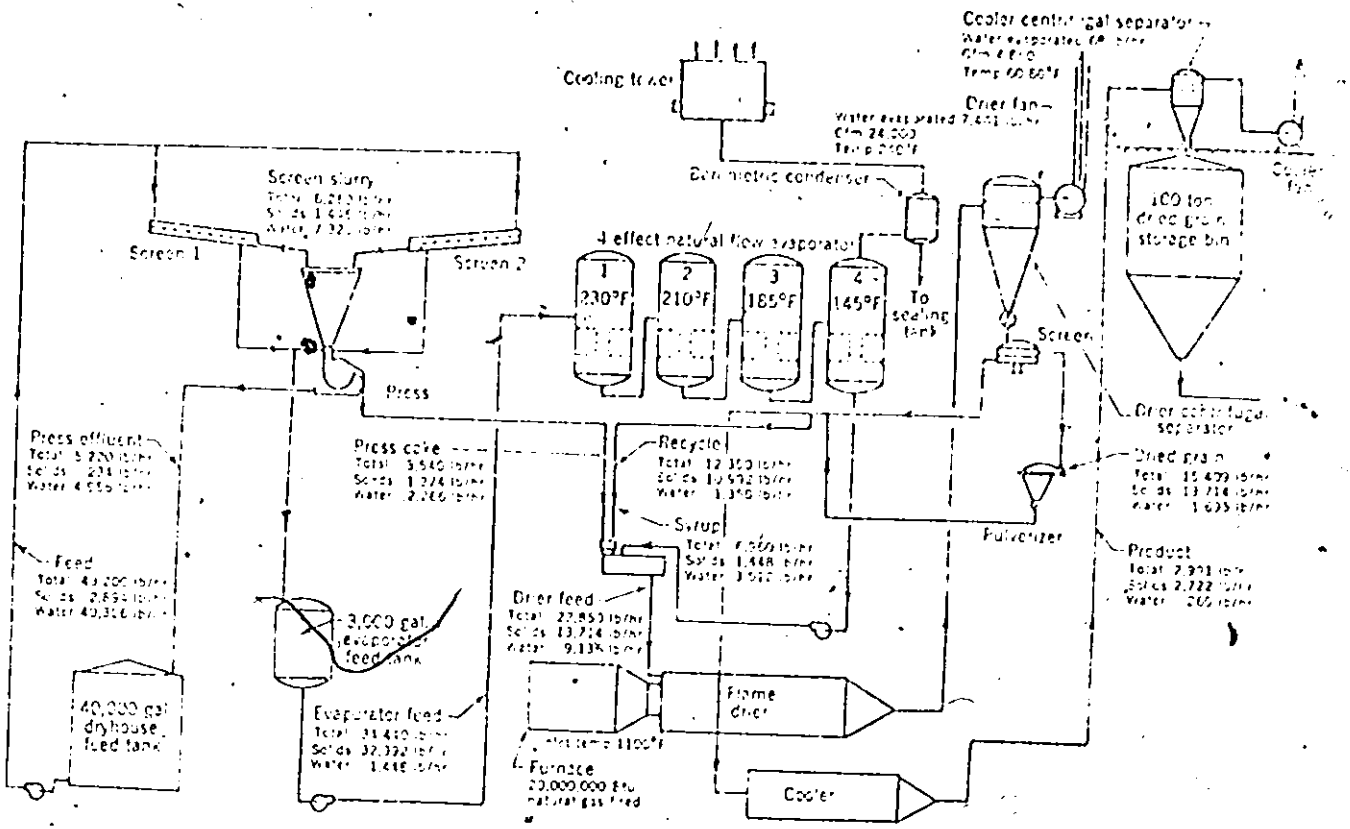

FIGURE 3.1: Typical Spent Grain Recovery System [3]

Dryers used for spent grains have been of two general types

1. Indirect Heat Cylindrical Rotary Shell Dryer

This class of dryer has the heating elements, often as steam jackets, well separated from the wet cake. An excellent product can be expected from such a system, but the production rate is low.

2. Direct-fired Cocurrent Rotary Dryer

This version is used more frequently because of better fuel economy and higher production rates [3]. In the direct fired, cocurrent, rotary dryer, the flames and the spent grain enter the unit at the same general location. As a result some searing and burning of the feed stock occurs. This produces the typical 'burnt' odor commonly associated with distilleries.

Along with the 'burnt' odor, the drying of a number of components which occur naturally in the grain can generate 'wet grain' or 'mash like' odors through volatilization. Neighborhood complaints are usually directed towards the burnt grain odor.

C. The Hiram Walker Process

It is generally agreed that the characteristic odor from the Hiram Walker plant is due to the drying of spent grain. The spent grain, containing roughly 6% solids, is dried according to the schemes shown in Figures 3.2 or 3.3, depending upon the plant operating mode. Spent grain from the stills is sent to centrifuges where solids are separated from the liquid. The liquid product with the distinct Hiram Walker odor passes through a four effect evaporator with a finishing pan. This step lowers the moisture content to about 60%.

The product from the evaporator, a thick peanut buttery syrup, and the solids portion from the centrifuges are conveyed to a flash dryer system. Each flash dryer, heated with natural gas, normally operates with a furnace temperature of 600°F. The drying process is designed to prevent the spent grain and the syrup from making direct contact with the gas flames. Drying is due to the hot excess air and combustion gases leaving the furnace section.

The Hiram Walker process involves three flash dryers. When they are operated in parallel, according to Figure 3.3, each dryer receives equal amounts of solids and syrup. When the plant is in the series mode, dryers 2 and 3 receive only

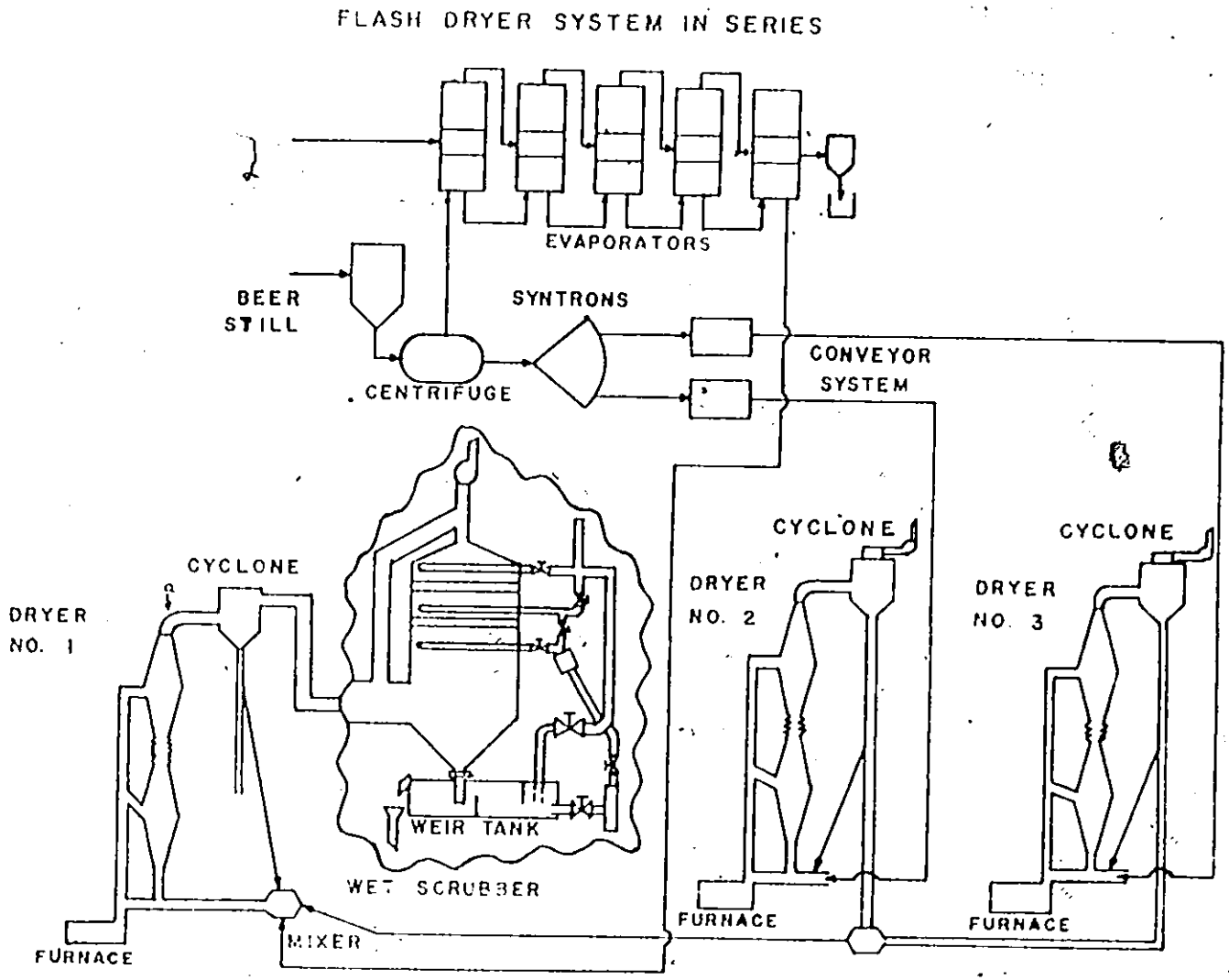

FIGURE 3,2: Series Flash Drying

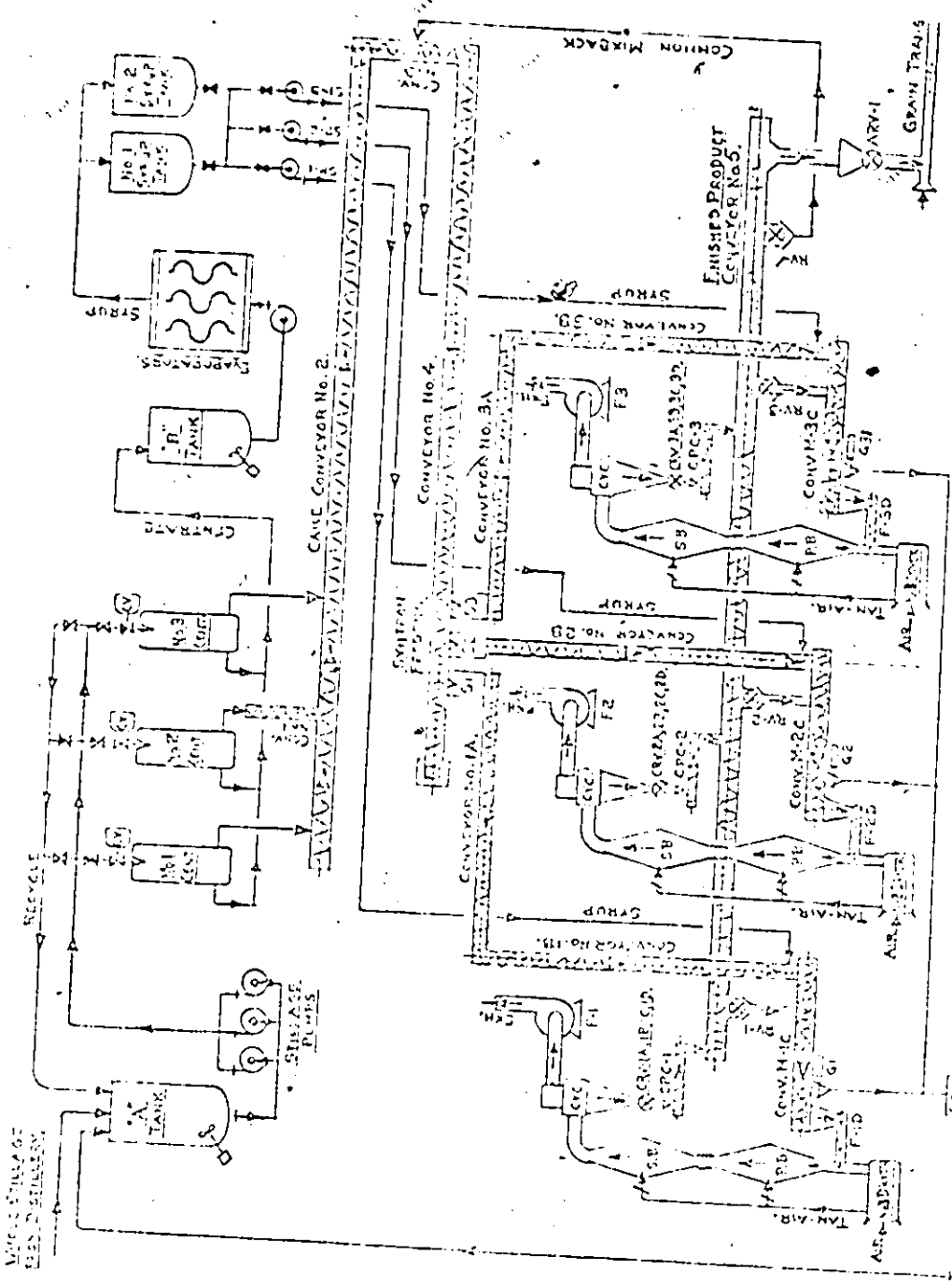

FIGURE 3.3: Parallel Flash Drying

the solids portion from the centrifuge whereas dryer 1 receives the end product of dryers 2 and 3 and all the syrup. It has been found that during series operation, most of the odor comes from dryer 1 [4].

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IV. SENSORY-ANALYTICAL METHODS FOR ODOR ANALYSIS

It has long been recognized that no analytical device is as sensitive to odors as the human nose. Therefore, ultimate judgements regarding odor acceptability will be, probably, always tempered by the presence of humans. Since analytical devices such as gas chromatographs, infrared, nuclear magnetic resonance and mass spectrometers, can provide, either individually or collectively, a chemical signature for a given odor, it was reasonable for researchers to attempt to combine the best features of the sensory and analytical systems. Investigations of this nature have generally attempted to isolate the odor causing chemicals by simultaneously smelling and analyzing an odor sample.

Before discussing previous applications of sensory-analytical techniques, it is useful to briefly review the basic principles of operation of the analytical methods themselves. Most of the instrumental concepts are well known. Literally dozens of excellent monographs are available for detailed information.

A. Analytical Methods

1. Gas Chromatography

Chromatography is a physical method of separation; in which the components to be isolated are distributed between

two phases as a result of a fluid moving through or along a stationary bed of large surface area.

In gas chromatography the moving phase is an inert gas carrying components which interact with the stationary phase or sorbent being used. Depending on the type of analysis to be carried out, two different sorbent types are available. If the sorbent is a solid of large surface area, the technique is called gas-solid chromatography (GSC). Gas liquid chromatography (GLC) utilizes a stationary phase consisting of a non-volatile liquid coated on an inert solid support. The GSC procedures are employed primarily in the separation of gases or relatively non-polar solutes of high volatility, whereas the GLC approach is more broadly applicable to a wider range of solutes.

The gas chromatographic technique involves injection of a sample through a self-sealing diaphragm into a packed column under conditions favoring volatilization of the compounds to be separated. A carrier gas moves these compounds along the column at rates which are dependent on their respective volatilities and interaction with the stationary phase. Consequently, different compounds are eluted from the column at different times. Flame ionization, electron capture or thermal conductivity detectors at the end of the column provide electrical signals corresponding to the passage of any specific compound towards the discharge side of the instrument.

2. Infrared Spectrometry

Infrared radiation is that part of the electromagnetic spectrum corresponding to energy with wavelengths longer than the visible range but shorter than the microwave region. Infrared radiation between 4000-660 cm^{-1} is useful for analytical purposes because it can be absorbed by organic materials and converted into energy of molecular vibration. The results of the interaction between infrared energy and organic species are spectral plots generally expressed in terms of intensity versus wavelength.

3. Nuclear Magnetic Resonance Spectrometry

Nuclear magnetic resonance (NMR) spectrometry depends upon interaction between an external magnet and magnetic nuclei, commonly hydrogen. Under appropriate conditions a sample can absorb electromagnetic radiation in the radio frequency region of 10 to 100 MHz. Since frequencies that can be absorbed are governed by the electronic environment in which hydrogen atoms are located in a sample, a typical NMR spectrum consists of a plot of frequencies of the adsorption peaks versus peak intensity and indicates the number and kind of hydrogens present.

4. Mass Spectrometry

In a mass spectrometer a sample is bombarded with an electron beam and the damage is recorded as a spectrum of

positive ion fragments and their relative abundance. By design, separation of the positive ion fragments is on a mass basis. The sample, as a vapor, diffuses into the low pressure system of the mass spectrometer where it is ionized with sufficient energy to cause fragmentation of the chemical bonds in the original molecules. The resulting positively charged ions are accelerated into a magnetic field which disperses them and permits relative abundance measurement of ions of a given mass-to-charge ratio.

In general, mass spectrometers consist of four major components, as shown in Figure 4.1. They are described briefly below:

a. a source for producing a beam of gaseous ions from the sample being analyzed
b. an analyzer for resolving the ion beam into its characteristic mass components according to the mass-to-charge ratios of the ions present
c. a detector for recording the relative abundance of each of the resolved ions
d. a vacuum system to provide the proper environment for all of the above processes.

The sample's volatility is the principal physical characteristic that dictates the route of sample introduction and also determines whether the sample is amenable to mass

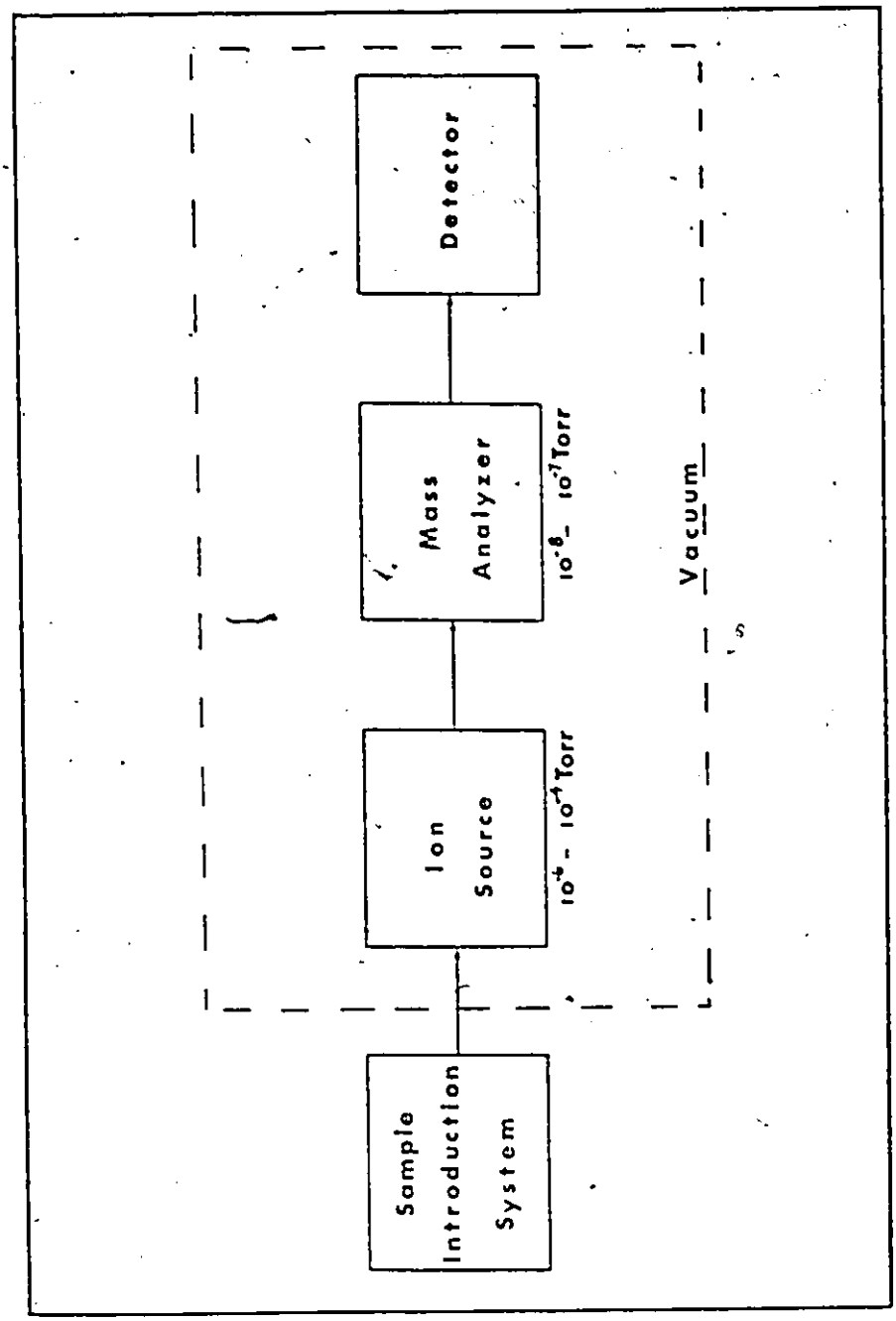

FIGURE 4.1: Schematic Diagram of a Mass Spectrometer System.

spectroscopic analysis. There are three main methods of introducing samples

i. Reservoir: If the compound has a vapour pressure of at least 10^{-2} mm Hg at 100-200°C then it can be injected into a heated reservoir that could be 2 to 3 ft from the ion source. The reservoir pressure, which is much higher than the ion source pressure, forces the sample vapor through a heated tube into the ion source

ii. Direct Inlet: Samples of extremely low volatility are introduced directly into the ion source

iii. Gas Chromatographic Coupling: Since interpretable mass spectra are best obtained with pure compounds, it would seem an obvious choice to use gas chromatography to provide samples for analysis. When combining a gas chromatograph with a mass spectrometer, there is a problem of transferring the compound in the gas chromatographic peak to the mass spectrometer ion source. Over the years, several different techniques have been developed to obtain mass spectrometric data of compounds eluting from a gas chromatographic column [1-6].

When suitable facilities are available, the effluent from the packed column is allowed to flow directly into the ion source by direct interfacing of GC/MS instruments. In the interfaced GC/MS system, the necessary pressure drop can be achieved by preferentially removing the carrier gas and then allowing the enriched sample into the mass spectrometer ion source.

When an interfaced GC/MS system is not available, then the simplest way of obtaining mass spectrum of an eluate is to collect the peak of interest by means of a cold trap and then transfer the sample to the mass spectrometer reservoir.

Another method of collecting and introducing small chromatographic samples into a mass spectrometer involves using small pieces of capillary tubing packed with gas chromatographic solid support to collect the fractions by adsorption of the compounds onto the packing. These small tubes can then be placed directly into the ion source through a vacuum lock.

B. Sensory-Analytical Methods

Chemical analysis, combined with sensory measurements, is an appropriate technique for gaining detailed information about any specific odor. However, such a sensory-analytical approach can not yet be considered to be a routine procedure. The unique description of a given odor, as

determined by a combination of human and instrumental capabilities, can, in principle, find application in both the regulatory and control aspects of odor pollution.

It is usually necessary to concentrate the odorous mixture prior to analysis on a gas chromatograph, infrared, NMR or mass spectrometer. The common methods of odor concentration involve freezing, adsorptive or absorptive sampling. Of the three, adsorptive sampling offers certain advantages in that many adsorbents adsorb little or no water while adequately picking up organic compounds [7]. A typical vapor collector, shown in Figure 4.2, utilizes five grams of chromosorb 102

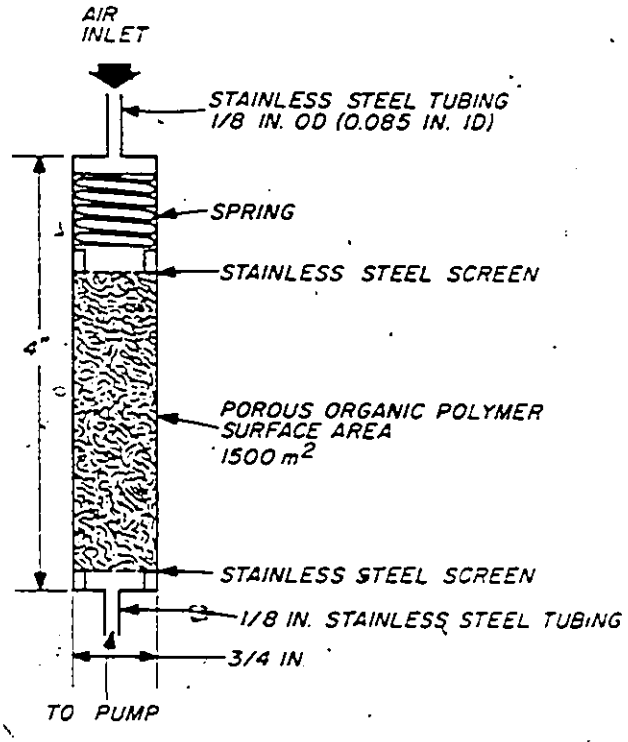

FIGURE 4.2: High-Speed Vapor Collector [7]

rather than activated carbon which adsorbs so strongly that subsequent recovery is made difficult. The collected vapors are removed by heating the system while flushing with a small stream of helium. The released organics are collected in a small diameter cooled tubing and then injected into a gas chromatograph for analysis. The GC system is shown in Figure 4.3

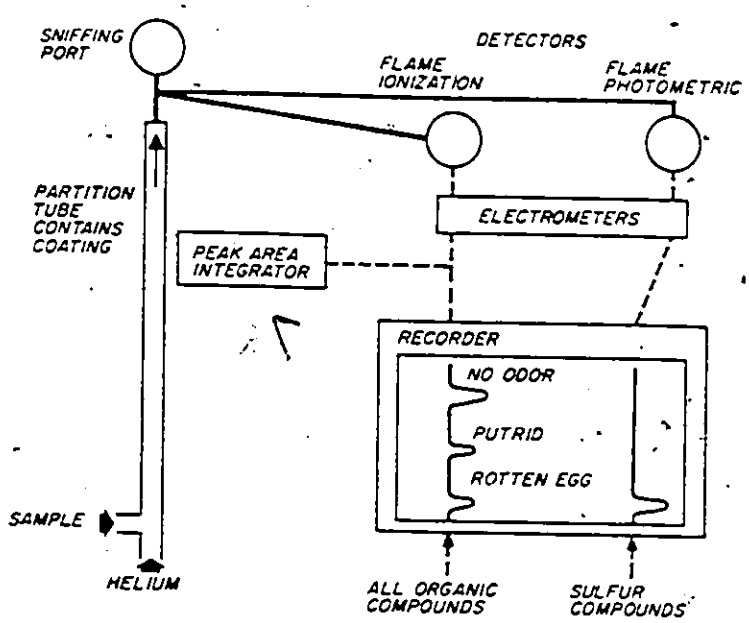

FIGURE 4.3: Schematic to Obtain an Odorgram [7]

The sniffing port permits smelling the components as they emerge from the column. The resulting chromatogram, with odorous peak approximately labelled, is frequently referred to as an odorgram.

This high speed vapor collector has been used by Dravnieks for investigation of air quality in schools [8] and in determinations of odorous components in tobacco smoke [9]. A similar device was employed by Arthur D. Little researchers when characterizing jet exhaust [10]. These investigators utilized pentane for extraction of the sample from the collector.

The application of mass spectrometry to odor analysis has been more limited. It has been pointed out that identification of odorants through mass spectrometry is possible, but very expensive [7]. There are also difficulties resulting from inadequate sample sizes and ambiguities in interpretation. Recently Reid et al [11] claim to have developed a Trace Atmospheric Gas Analyzer technique in which they use a mass spectrometer system to identify and quantify ultra-trace species in gases at atmospheric pressure.

An example of the potential of sensory-analytical methods for odor analysis is provided by the EPA supported work on rendering plant odors [12].

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V. RESULTS OF ODOR ANALYSIS

Since it is believed that the odorous compounds in the Hiram Walker emissions originate from the syrup sent to the flash dryer, this syrup was used to generate an odor that was subsequently analyzed in detail. For this analysis, a combination of gas chromatography, mass, infrared and nuclear magnetic resonance spectrometry was employed in an effort to fingerprint the odors.

The syrup used for generating odors was obtained from Hiram Walker and Sons Limited. The sample was collected essentially at the entrance to the multiple effect evaporation unit as shown in Figure.5.1 by point 7 .

A. Procedures for Generating Odor Samples

Two techniques were used to generate odor samples;

1. Extraction Method:

In the extraction procedure, odorous components were recovered over a sixteen hour period from two hundred grams of syrup in a soxhlet extractor. The odorants were concentrated in a distillation column by removal of the acetone, ether or tetrahydrofuran extraction agents.

2. Adsorption Method:

This procedure utilized an adsorption concentrator designed on the basis of units used by previous researchers

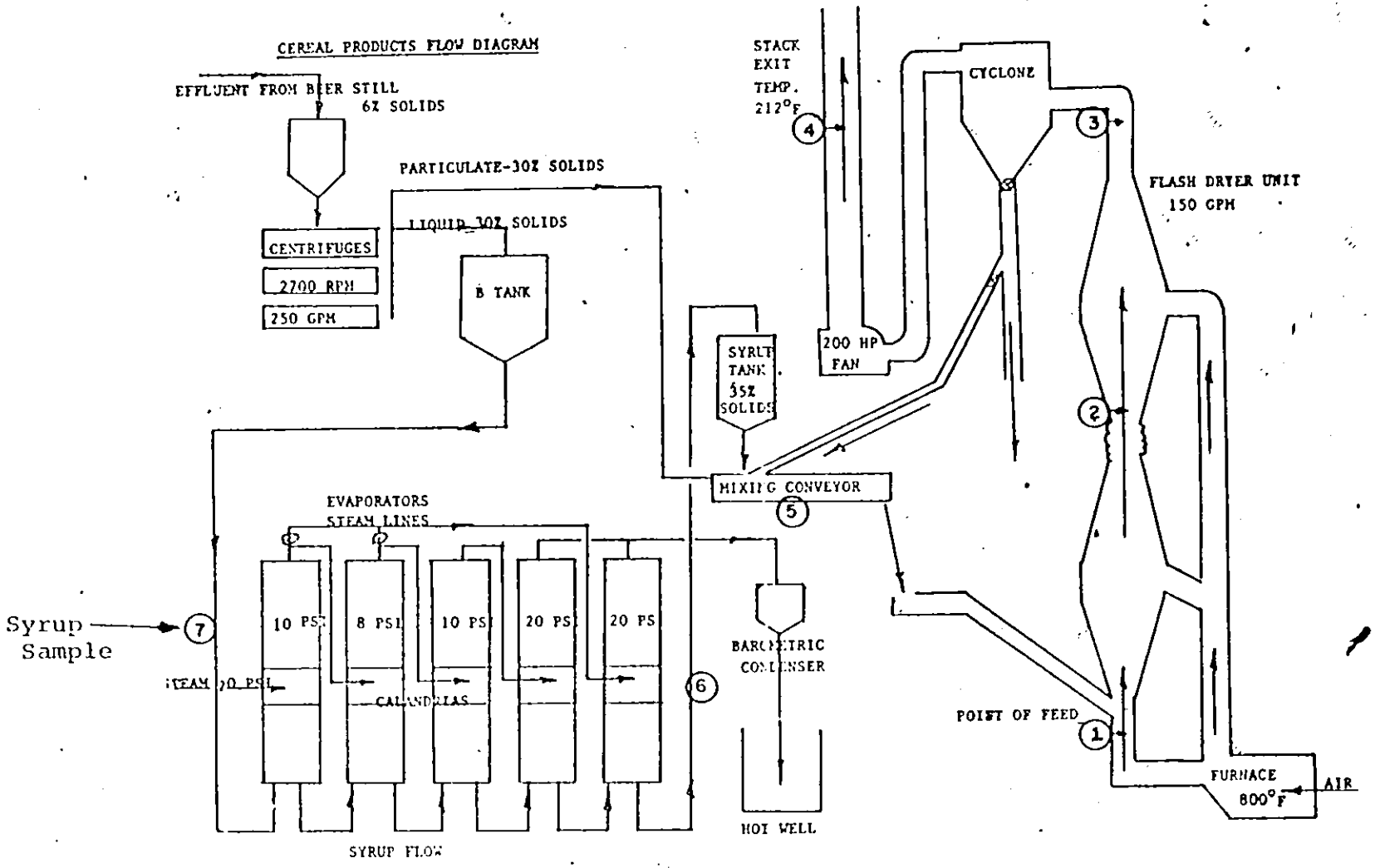

FIGURE 5.1: Location of Sampling Points in Flash Dryer System

[1, 2, 3]. The concentrator shown in Figure 5.2 was filled with Apiezon L. Preliminary experimentation with the gas chromatograph demonstrated that this material was a reasonably nonselective adsorbent.

The odor generation technique with the concentrator simply involved passing nitrogen continuously through the syrup which was maintained at 150°C in an oil bath. The compounds carried by the nitrogen to the concentrator were first passed through a knockout trap to remove as much water as possible according to Figure 5.3. The concentration procedure was continued until an odor could be detected from the exit of the concentrator.

B. Results of Odorous Sample Analyses

1. Infrared Analysis

An odor sample obtained by the extraction procedure was subjected to analysis on a Beckman IR 12 Infrared Spectrometer. From the spectrum shown in Figure 5.4, there appear to be no primary amines, nitrates, mercaptans or halogens present in the odor sample. The peak at 912 cm^{-1} is possibly due to the solvent tetrahydrofuran. The peaks at 1164 cm^{-1} and the coupled peaks around 1250 and 1275 cm^{-1} suggest the presence of esters and long chain fatty acids. Indication of

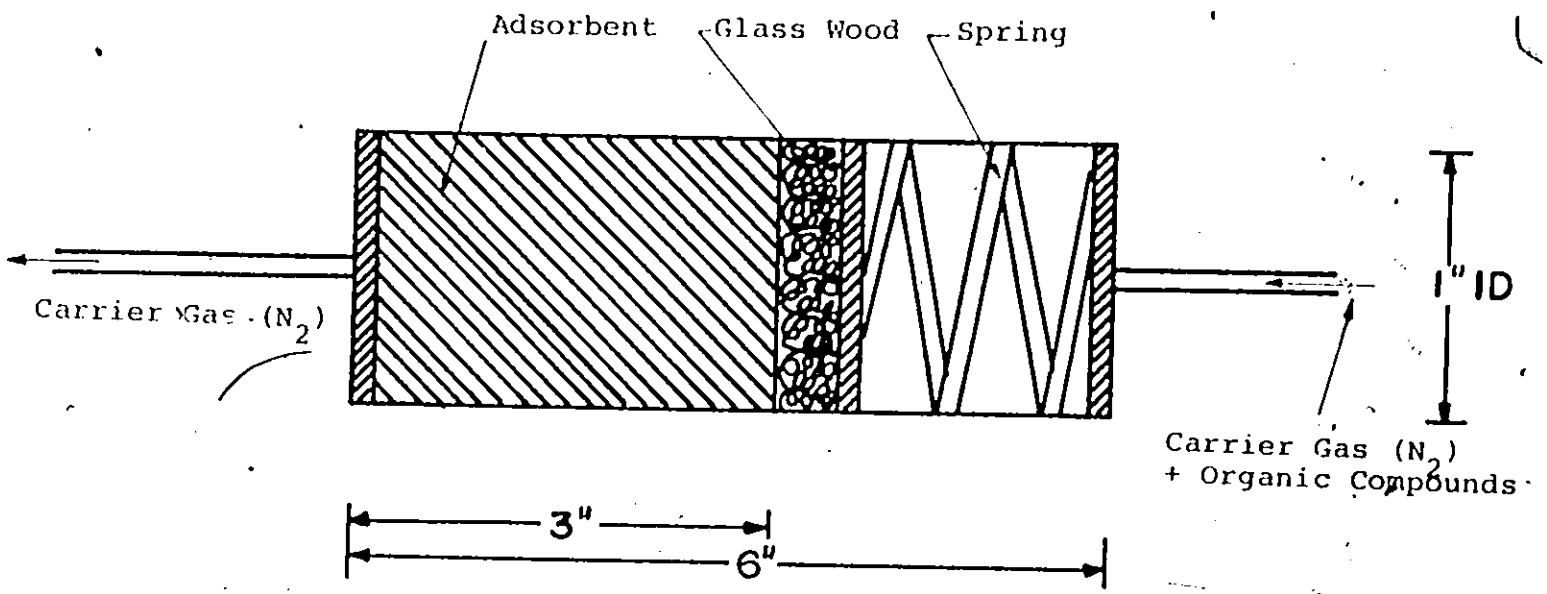

FIGURE 5.2: The Concentrator

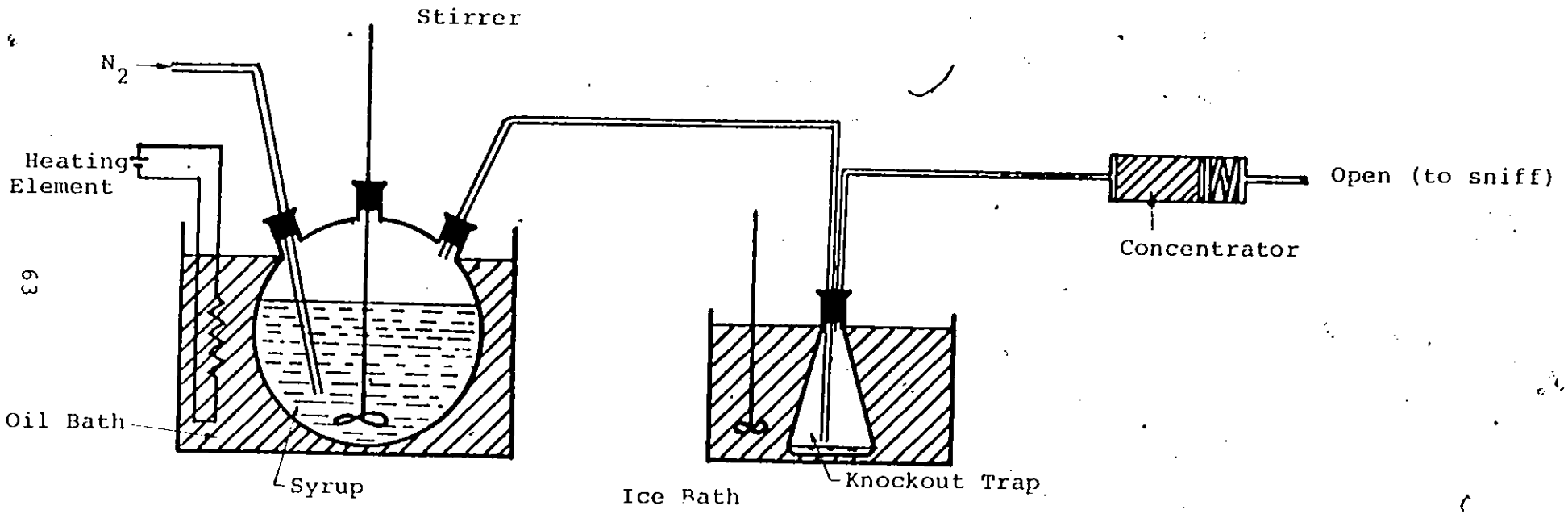

FIGURE 5.3: The Concentrator Train

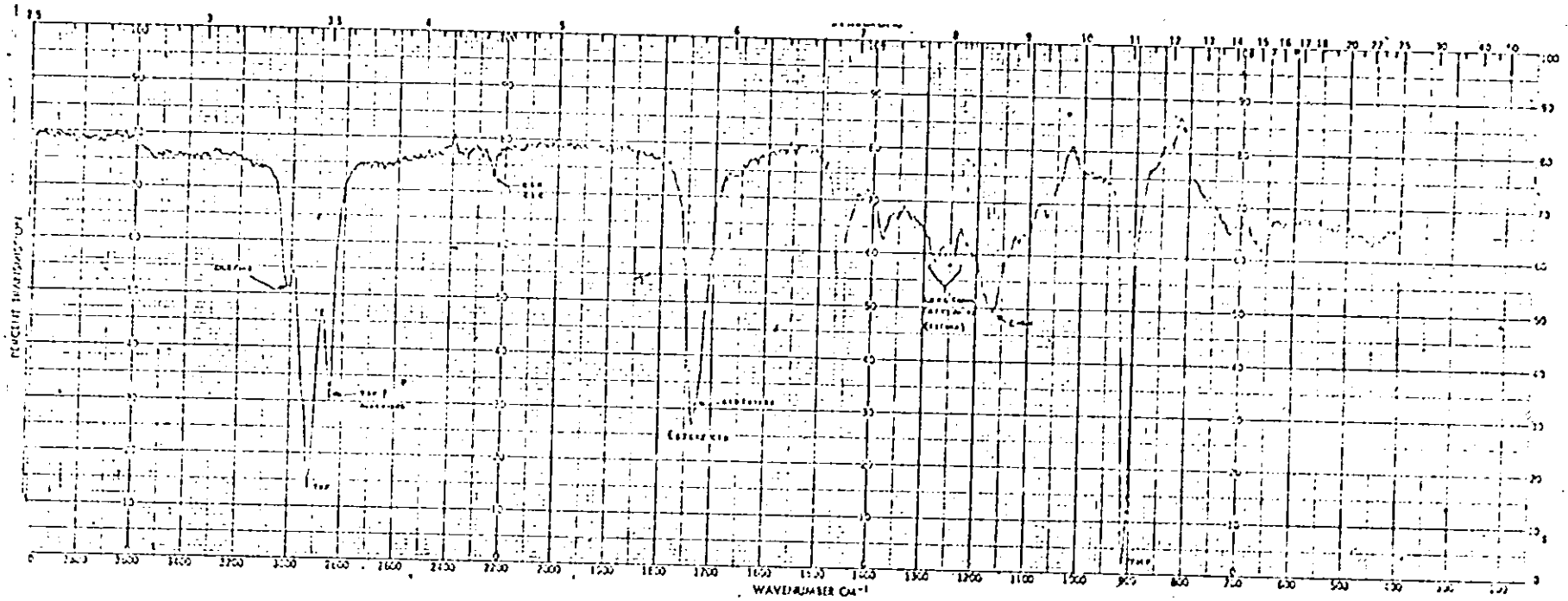

FIGURE 5.4: Infrared Spectrum of Odorous Sample

the presence of C=O esters (possibly α, β-unsaturated aryl esters) and aldehydes is provided by the peak near 1735 cm^{-1}. The peak at 2240 cm^{-1} indicates the presence of C≡C or C≡N bonds. Tetrahydrofuran could possibly be responsible for the peak at 2842 cm^{-1}, as well as for the peak around 2910 cm^{-1}. Olefins or aromatics could be associated with the peak at 3005 cm^{-1}.

2. Nuclear Magnetic Resonance (NMR) Analysis

An extraction type sample was run in a JOEL C-60 HL spectrometer. Since the spectrum in Figure 5.5 shows no peak between 6 and 8δ, it is safe to assume that no benzene rings were present. If such rings were present a deflection should have appeared at about 8δ. The spectrum also indicates that double bonds may be present, but the deflection at 5.38δ could also be due to the presence of tetrahydrofuran.

3. Gas Chromatographic Analysis

The gas chromatograph used for analysis of odors was a Varian 1520 programmable unit. Initial chromatographic runs were made with an odor sample obtained using the extraction procedure. Many different columns, including PPE, FFAP, DC550,

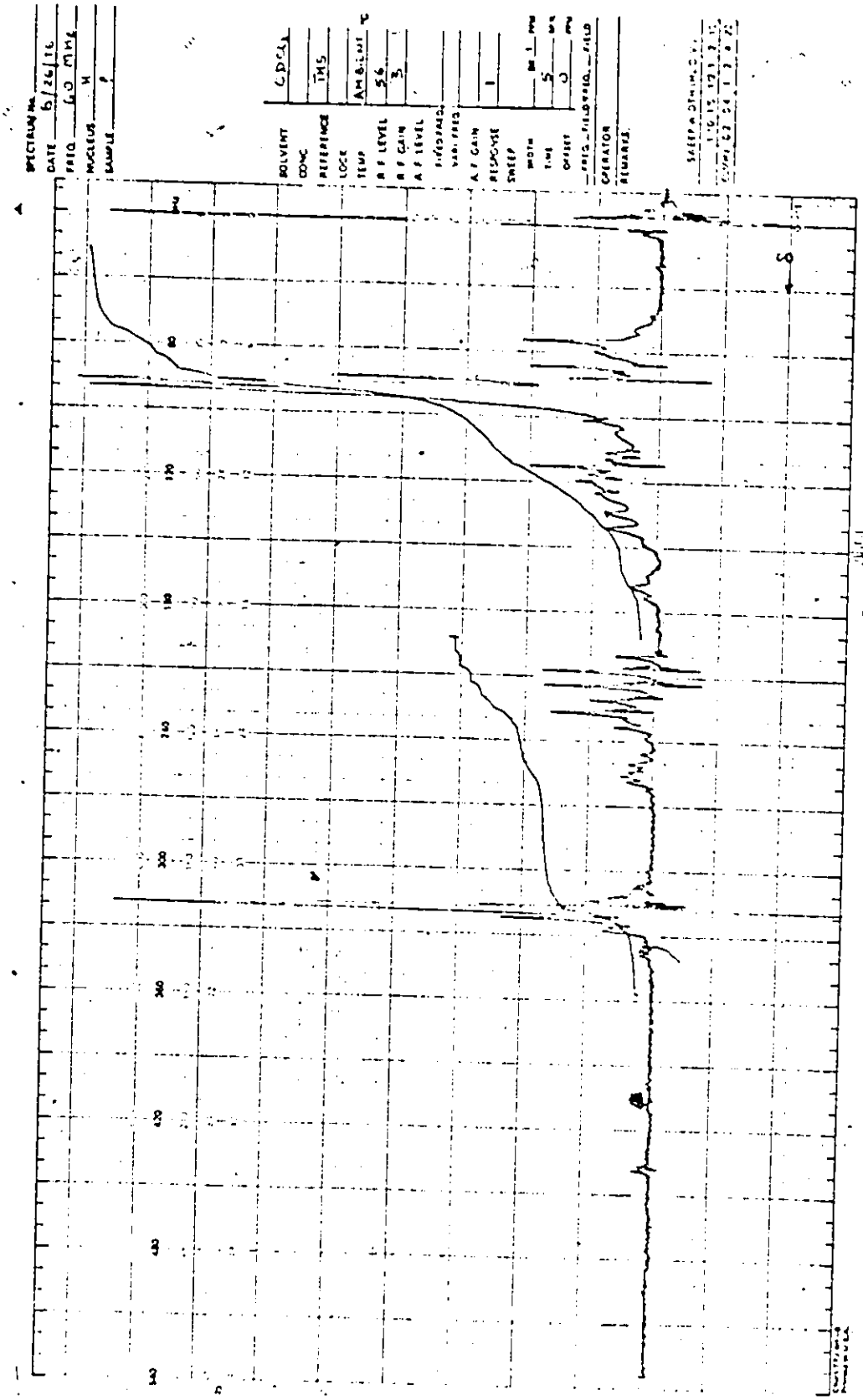

FIGURE 5.5: NMR Spectrum of Odorous Sample

SE 30 and Apiezon L, were tried. A PPE column chromatogram is shown in Figure 5.6. Comparison with the Apiezon L chromatogram illustrated in Figure 5.7, indicates that Apiezon L provided a better separation.

The extraction method of odor acquisition was found to be generally inferior to the adsorption technique because resolutions were not as good with the extraction method.

The ultimate gas chromatographic analysis was performed with the splitter arrangement for odor sniffing shown in Figure 5.8. Since the lengths of tubes A and B were identical it was possible to simultaneously sniff at port C as soon as a compound appeared on the chromatograph recorder. This splitter system was later used to collect samples for mass spectrometric analysis.

Figures 5.9 and 5.10 are representative of the results obtained using the splitter equipped gas chromatograph. Figure 5.9 depicts the characteristics of odor sample generated through adsorption while Figure 5.10 illustrates those of specimens acquired through the extraction procedure. Both indicate that there are at least ten major odorous peaks. The hedonic qualities of the odorous peaks in Figure 5.10 are listed in Table 5.1.

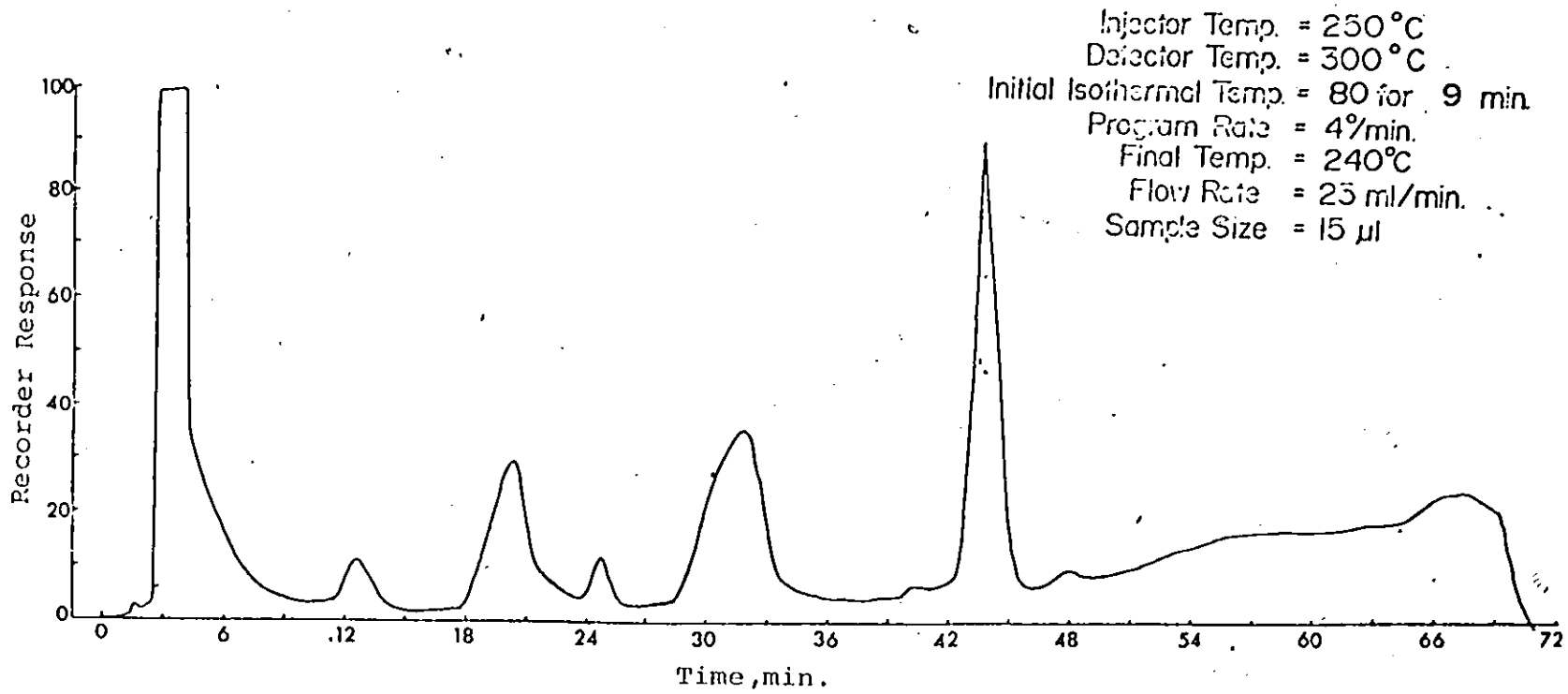

FIGURE 5.6: Gas Chromatogram of Odorous Sample Using 8% PPE Column

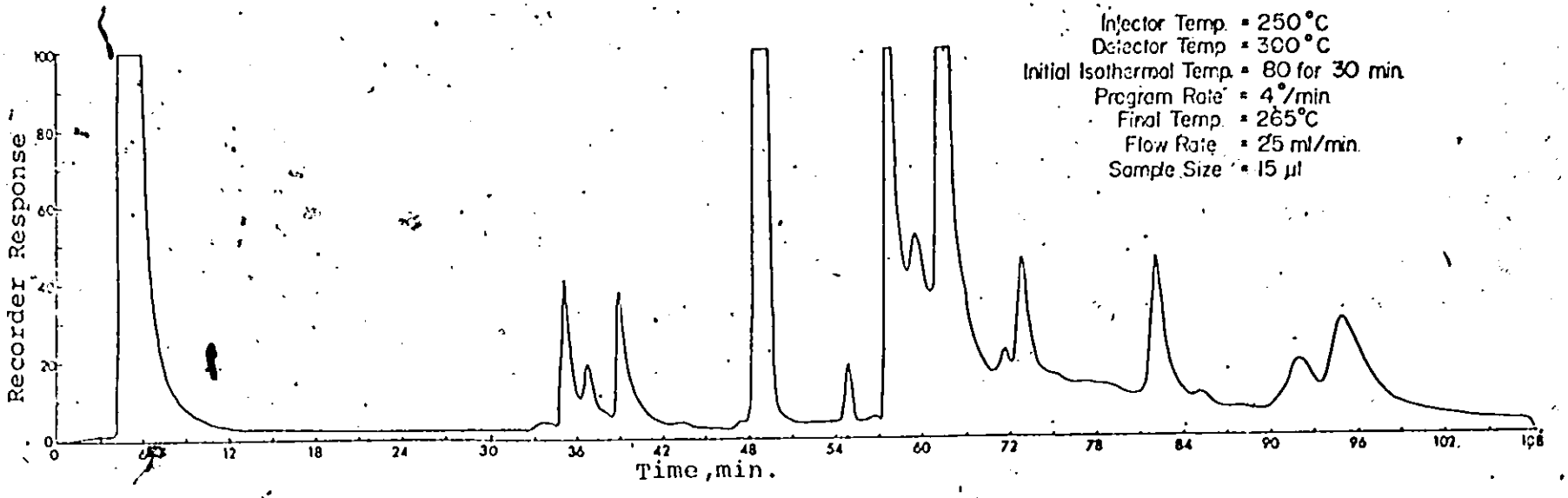

FIGURE 5.7: Gas Chromatogram of Odorous Sample Using 10% Apiezon L Column

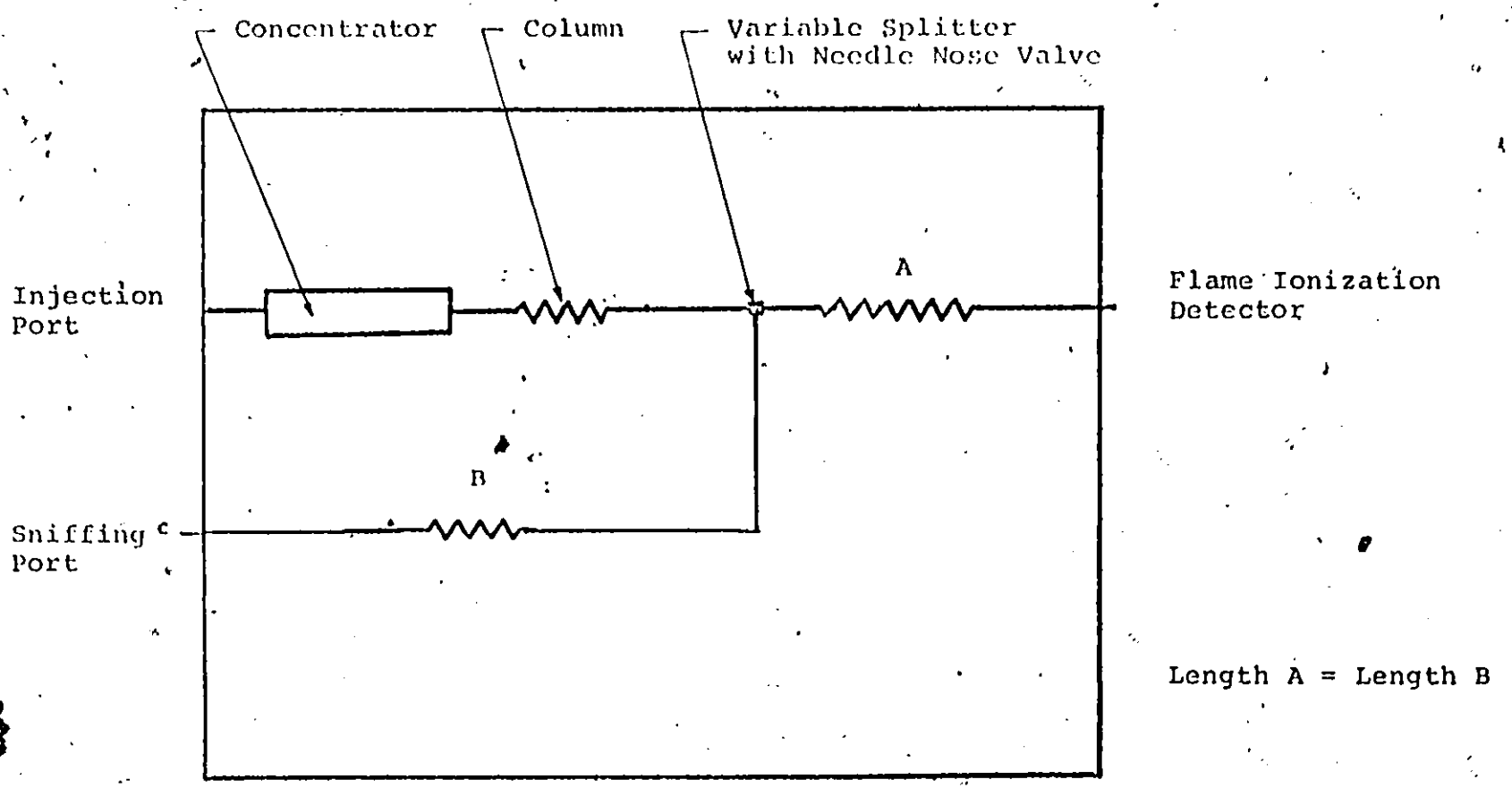

FIGURE 5.8: Schematic of the Inside of the Gas Chromatogram with the Splitter Arrangement

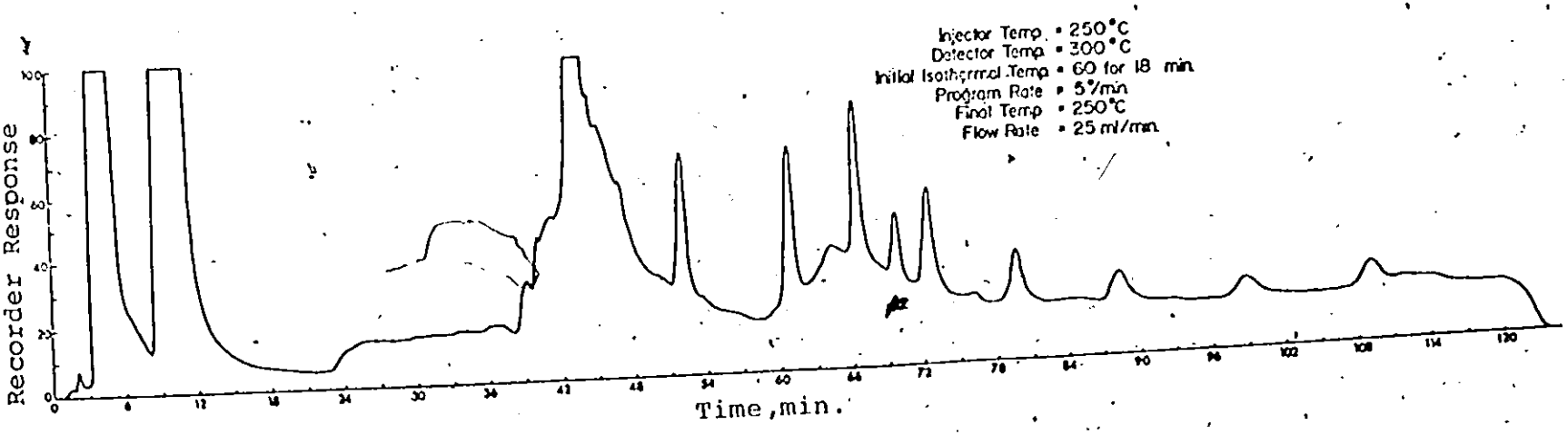

FIGURE 5.9: Gas Chromatogram of Odorous Sample Generated Through Adsorption Using 10% Apiezon L Column

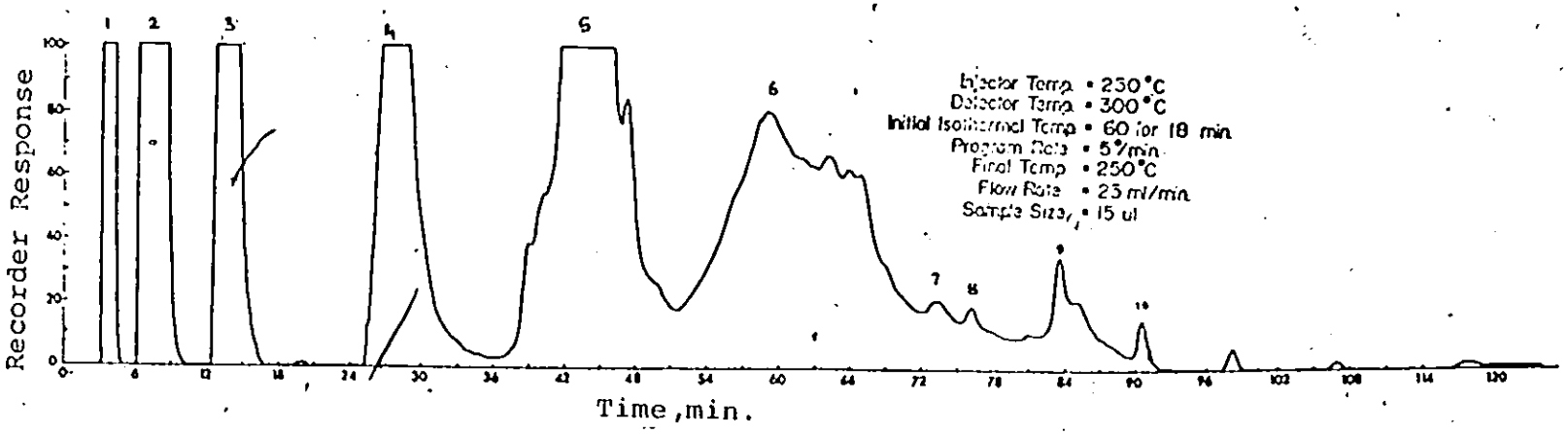

FIGURE 5.10: Gas Chromatogram of Odorous Sample Generated Through Extraction Using 10% Apiezon L Column

Peak No.	Peak Appearance, Time, min*	Temperature °C	Odor Property	Mass Spectrometer Scan Number
1	3.0	60	Extraction Agent Smell	No MS
2	6.5	60	Some	No MS
3	12.0	60	Sweet, Pleasant	--
4a	25.5	97.5	Sweet-Acetate Type	4.1, 4.2, 4.3, 4.4
b	27.5	107.5	Alcoholic	4.5, 4.6
c	30.0	120	Alcoholic	4.7, 4.8, 4.9, 4.10
5a	37.5	157.5	Fruity, Slightly Burnt	5.1
b	40.0	170	Hard to Detect	--
c	43.0	185	Sweet	5.2, 5.3
d	46.0	200	Strongly Alcoholic	5.4
6a	51.0	240	Burnt	--
b	61.5	250	Burnt	6.1
7	72.0	250	Burnt	--
8	76.0	250	Burnt	--
9	83.0	250	Burnt	--
10	90.0	250	Undefinable	10.1

*This time represents time at which collection of MS sample was initiated. Samples were collected for a maximum period of three minutes.

TABLE 5.1: Hedonic Properties of Gas Chromatograph Peaks From Extraction Type Odor Samples Used for Mass Spectrometric Analysis

4. Mass Spectrometric Analysis

The extraction technique was used to obtain a concentrated sample for the gas chromatographic-mass spectrometric analysis. It was found that a larger amount of material corresponding to any gas chromatographic peak could be collected when concentrated extraction type samples were used rather than those acquired according to the adsorption collection technique.

The system used for collecting the samples coming out of the gas chromatographic splitter is shown in Figure 5.11.

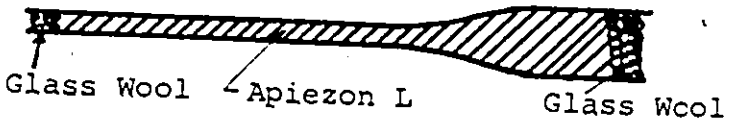

FIGURE 5.11: Collector for Introduction to Mass Spectrometer

As soon as a peak appeared on the recorder, sampling was initiated. Since there was no appropriate technique for establishing

the gas chromatographic resolution needed for subsequent mass spectrometric analysis, several successive collections of the major peaks were made. Because up to four samples were collected from some of the peaks a total of sixteen specimens were available for mass spectrometric analysis, as shown in Table 5.1.

A major change had to be made in the mass spectrometer in order to introduce the samples. This modification is shown in Figure 5.12. Introduction of the sample was accomplished by first freezing it in a thimble kept in a liquid nitrogen bath. Valves 1, 2, 3 and 4 were then opened and the system evacuated to 10^{-6} Torr. Since the mass spectrometer operates at a pressure of 10^{-6} Torr, the system must be evacuated to that level in order to get any meaningful results. In addition, this high vacuum insures the removal of any residuals from previous samples and vaporization of any compounds that may have very low volatility. After the system had been evacuated, Valve 3 was closed and the liquid nitrogen bath was moved from the thimble to the cold thumb. This was necessary to permit sample vaporization and subsequent trapping in the cold thumb. After the system had reached 10^{-6} Torr pressure again, the liquid nitrogen was removed and the computer associated with the mass spectrometer started scanning and acquiring data.

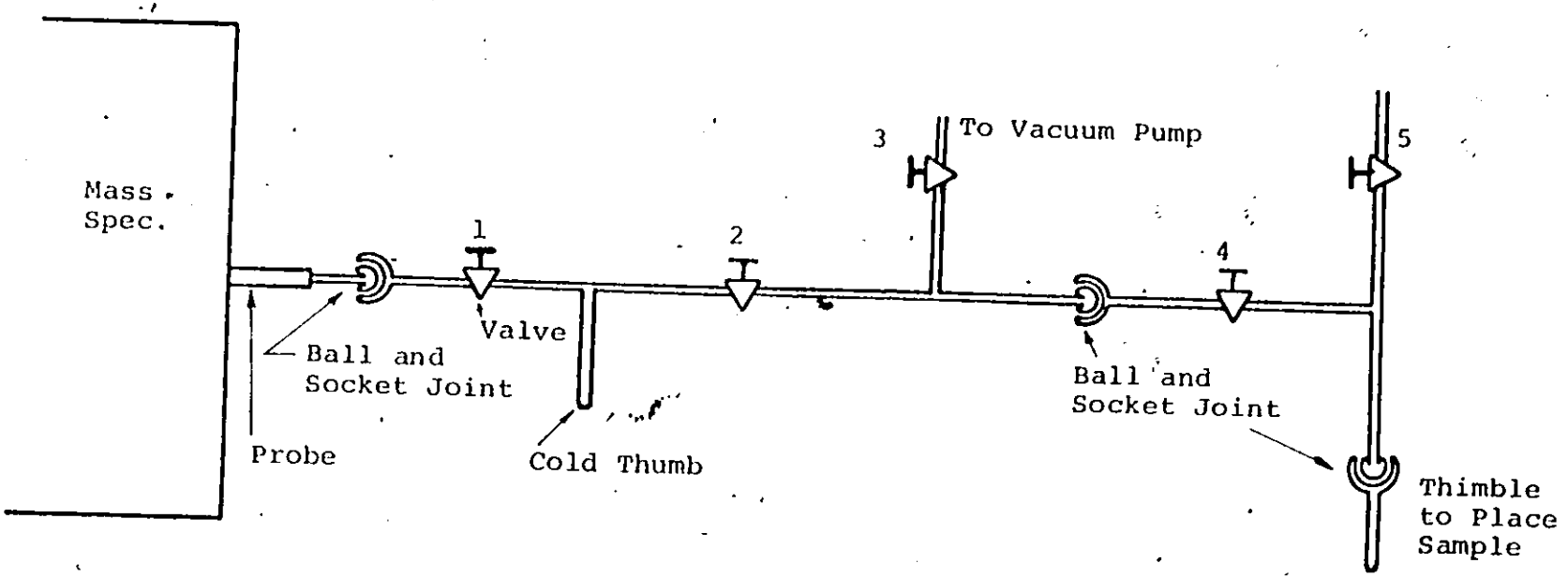

FIGURE 5.12: System Used to Introduce Sample Into Mass Spectrometer

Fourteen samples were run in a Varian CH5 double focussing mass spectrometer. Unfortunately the run for GC peak No. 3 was ruined due to leaks in the introduction system. Because of leaks and lack of sufficient sample in the collector, the major MS peaks for GC samples, 5b, 6a, 7, 8 and 9 of Table 5.1, were suppressed to such an extent that no significant results could be obtained.

Typical MS scan results are given in Tables 5.2 to 5.5. Each scan provides mass per unit charge (m/e) under the heading of MASS. The intensity of each peak is designated by INT. In addition, the percent relative abundance of each mass is designated by % RA on the basis of maximum intensity being given a value of 100. Also values of percent total intensity (% TI) are calculated directly from the intensity figures in the last column. It is immediately obvious from these results that complete identification of the odorous compounds would be impossible due to the large number of peaks involved. This problem arises from the poor resolution of the compounds by the gas chromatograph. It would appear that inadequate separation by the gas chromatograph led to too complex a mixture as the input to the mass spectrometer. When too complex a mixture is fed into a mass spectrometer the results cannot be analysed to the extent of precisely identifying specific components.

[illegible] SAMPLE FILE: 1359[illegible] SCAN 2
DATE: 07/22/76 TIME: 1356 CALIB. NO.: 0736 PEAK TIME: 1:56
SAMPLE: 5-3 COST /L: 26 TOTAL IONIZATION: 294415.

IONIZATION: CHS FORMULA: DIBROM WEIGHT: 0.000
ANALYST: PDC SUBMITTED BY: BENTRA ACCT. NO.: 109110

REQUESTED RESOLUTION: 1500 THRESHOLD: 2 MINIMUM WIDTH: 2
MEASURED SCAN TIME: 3.0 SEC SAMP. INTVL.: 0.250 MSEC. MINIMUM AREA: 2

10 CHROMATIC DOME SCANS ACQUIRED
SCAN NOS: 10 SCAN TIME (SECS.) UP: 3.6 TOP: 7.0
HIGH MASS: [illegible] PEAK: 20.0 BOTTOM: 0.0
94 PEAKS FOUND FROM FILE, 10 PEAKS ASSIGNED MASSES
[illegible] REFERENCE PEAKS FOUND BASELINE 18 AND 855 AMU

PEAK NO.	MASS	% RA	% TI	INT
12	19.93	0.53	0.01	24.
13	24.96	6.39	0.10	285.
14	25.96	3.10	0.77	2276.
15	26.96	3.96	0.99	2912.
16	27.96 HS	100.00	24.96	73472.
17	28.96	2.31	0.58	1694.
18	29.99	0.55	0.14	407.
19	29.96	0.07	0.02	52.
20	30.96	0.29	0.06	189.
21	31.93	26.90	6.49	19153.
22	33.96	0.06	0.01	44.
23	34.93	7.47	1.86	5488.
24	35.93	1.17	0.28	863.
25	36.93 F	2.45	0.61	1796.

TABLE 5.2: Results for Mass Spectrometer Run 4.1, for Gas Chromatograph Peak 4

... continued

PEAK No.	MASS	% RA	% TI	INT
26	36.96 F	1.39	0.35	1022.
27	37.93	0.18	0.05	135.
28	37.96	1.49	0.37	1092.
29	38.99	2.61	0.65	1914.
30	39.90	2.09	0.52	1538.
31	39.99	0.32	0.08	235.
32	40.93	0.14	0.04	104.
33	40.96 F	0.50	0.13	370.
34	40.99 F	0.65	0.16	479.
35	41.43	0.33	0.06	240.
36	41.96	4.72	1.18	3466.
37	41.99	0.01	0.00	7.
38	42.43	0.10	0.03	77.
39	42.96	56.53	14.11	41535.
40	43.93 F	8.87	2.21	6520.
41	43.96 F	1.04	0.26	765.
42	44.93	0.02	0.00	12.
43	44.96	0.11	0.03	82.
44	46.93	19.73	4.92	14495.
45	47.93	7.46	1.86	5480.
46	48.93	6.26	1.56	4600.
47	49.93	2.25	0.56	1650.
48	50.93	0.08	0.02	60.
49	50.99	0.02	0.01	18.
50	52.96	0.12	0.03	88.
51	54.96	0.18	0.04	132.
52	56.99	0.38	0.10	281.
53	57.96	0.03	0.01	22.
54	57.99	11.32	2.83	8320.
55	58.03	0.05	0.01	35.

TABLE 5.2: Results for Mass Spectrometer Run 4.1, for Gas Chromatograph Peak 4

... continued

PEAK NO.	MASS	% AA	% AI	I/T
56	58.99	0.39	0.10	290.
57	60.93	0.03	0.01	22.
58	69.87	0.73	0.18	538.
59	71.87	0.29	0.07	216.
60	72.99	0.53	0.13	392.
61	73.87	0.14	0.04	106.
62	74.93	0.03	0.01	23.
63	76.93	0.13	0.03	96.
64	81.87	1.97	0.49	1450.
65	82.87	52.61	13.13	38655.
66	83.87	1.94	0.48	1422.
67	84.87	33.80	8.43	24831.
68	85.87	0.42	0.10	305.
69	86.87	5.11	1.25	3680.
70	88.93	0.03	0.01	21.
71	98.87	0.03	0.01	23.
72	104.87	0.03	0.01	23.
73	116.81	0.42	0.11	310.
74	117.81	1.62	0.40	1186.
75	118.81	0.43	0.11	314.
76	116.93	0.07	0.02	53.
77	119.91	1.26	0.31	924.
78	120.81	0.03	0.01	19.
79	121.81	0.34	0.09	253.
80	126.81	0.01	0.00	4.
81	127.78	0.02	0.01	16.
82	129.84	0.04	0.01	32.
83	141.84	0.03	0.01	23.
84	146.93	0.04	0.01	32.
85	192.87	0.03	0.01	24.
86	206.90	0.03	0.01	20.

TABLE 5.2: Results for Mass Spectrometer Run 4.1, for Gas Chromatograph Peak 4

LOW RESOLUTION MASSES SAMPLE RUN: 1359ENG607 SCAN 6
DATE: 07/22/76 TIME: 1358 CALIB. RUN: 073D RET. TIME: 3:00
SAMPLE: 5-3 BASE M/E: 281 TOTAL IONIZATION: 1736140.

INSTRUMENT: CH5 FORMULA: UNKNOWN WEIGHT: 0.000
ANALYST: RDC SUBMITTED BY: BENTRA ACCT. NO.: 109110

REQUESTED RESOLUTION: 1500 THRESHOLD: 2 MINIMUM WIDTH: 2
MEASURED SCAN TIME: 0.0 SEC SAMP. INTVL.: 0.250 MSEC. MINIMUM AREA: 2

10 QUADRATIC DOWN SCANS ACQUIRED
LOW MASS: 10 SCAN TIMES (SECS.) UP: 3.0 TOP: 7.0
HIGH MASS: 900 DOWN: 20.0 BOTTOM: 0.0
361 PEAKS READ FROM FILE, 566 PEAKS ASSIGNED MASSES
72 OF *-2 REFERENCE PEAKS FOUND BETWEEN 18 AND 855 AMU
LIST THRESHOLD = 1.00 % RELATIVE ABUNDANCE

PEAK NO.	MASS	% RA	% TI	HT
2	24.62 F	3.46	0.58	10015.
3	24.78 F	1.76	0.29	5112.
12	25.12 F	1.57	0.26	4536.
34	26.06 F	1.16	0.19	3368.
37	26.37 F	2.92	0.49	8448.
40	26.62 F	1.70	0.28	4935.
41	27.65 FM	27.65	4.62	80127.
43	118.93	1.11	0.19	3216.
56	124.90 F	6.60	1.10	19135.
58	125.40	1.57	0.26	4560.
60	125.90 F	1.54	0.26	4456.
74	132.93 FM	23.06	3.85	66815.

TABLE 5.3: Results for Mass Spectrometer Run 4.4, for Gas Chromatograph Peak 4

PEAK No.	MASS	% RA	% TI	INT
77	133.43	5.50	0.92	15951.
78	133.93	4.22	0.70	12223.
80	134.90	1.40	0.23	4044.
102	146.84 F	1.24	0.21	3596.
133	162.87	2.29	0.38	6624.
135	164.87	1.63	0.27	4728.
151	176.90	5.60	0.94	16239.
153	177.87	1.53	0.25	4424.
155	178.90	3.82	0.64	11055.
163	186.90	1.52	0.25	4392.
168	190.90	17.38	2.90	50367.
173	191.90 F	3.89	0.65	11263.
177	192.87 F	13.65	2.28	39551.
181	193.87	2.91	0.49	8432.
182	194.87	1.41	0.23	4076.
191	202.87	1.52	0.25	4400.
194	204.90 F	5.79	0.97	16767.
197	205.90	1.38	0.23	4008.
202	206.90 FM	32.73	5.46	94847.
207	207.90	6.58	1.10	19071.
212	208.90	3.79	0.63	10991.
226	220.96 F	1.39	0.23	4028.
240	234.84	2.70	0.45	7832.
253	248.87	16.92	2.82	49023.
256	249.87	4.68	0.78	13567.
260	250.87	10.76	1.80	31167.
262	251.87	2.59	0.43	7520.
264	252.87	1.60	0.27	4632.
274	264.87 F	21.86	3.65	63359.
277	265.90	5.34	0.89	15487.
281	266.90	10.78	1.80	31231.

TABLE 5.3: Results for Mass Spectrometer Run 4.4, for Gas Chromatograph Peak 4

PEAK NO.	MASS	% RA	% TI	HT
284	267.90	2.40	0.40	6968.
286	268.87	1.55	0.26	4496.
300	280.93 PKS	100.00	16.69	289791.
305	281.90 PKS	78.89	13.17	228607.
310	282.90 PKS	65.46	10.93	189695.
314	283.90	13.60	2.27	39423.
317	284.90	4.44	0.74	12863.
346	354.90	9.20	1.54	26655.
348	355.90	3.52	0.59	10191.
349	356.90	2.40	0.40	6968.

TABLE 5.3: Results for Mass Spectrometer Run 4.4, for Gas Chromatograph Peak 4

LOW RESOLUTION MASSES SAMPLE RUN: 1372EHG607 SCAN: 1 6
DATE: 07/22/76 TIME: 1752 CALIB. RUN: 0730 RET. TIME: 3:00
SAMPLE: 8-6 BASE P/S: 18 TOTAL IONIZATION: 120037.

PEAK NO.	MASS	% RA	% TI	INT
1	11.99?	0.24	0.13	155.
2	14.99?	0.36	0.21	250.
3	15.96?	4.24	2.31	2776.
4	15.99?	0.21	0.11	136.
5	16.99?	59.36	32.42	38911.
6	16.99?	0.07	0.04	44.
7	17.99 S	100.00	54.60	65535.
8	18.99	0.18	0.10	119.
9	19.99	0.52	0.28	338.
10	26.99	0.11	0.06	75.
11	27.96	4.12	2.25	2700.
12	28.93	0.03	0.01	17.
13	28.96	0.02	0.01	10.
14	30.99	0.06	0.03	37.
15	31.96	0.89	0.49	585.
16	35.93	0.02	0.01	16.
17	39.99	0.03	0.02	21.
18	41.99	0.07	0.04	44.
19	42.99	1.23	0.67	808.
20	43.96	1.66	0.91	1090.
21	43.99	0.02	0.01	14.
22	58.03	0.24	0.13	158.
23	58.99	0.06	0.03	40.
24	70.03	0.05	0.03	31.
25	71.87	0.02	0.01	14.

TABLE 5.4: Results for Mass Spectrometer Run 5.1, for Gas Chromatograph Peak 5

... continued ...

PEAK No.	MASS	% RA	% TI	INT
26	73.03	0.56	0.31	379.
27	77.87	0.08	0.04	52.
28	79.87	0.03	0.02	22.
29	80.90	0.05	0.03	33.
30	81.87	0.08	0.05	55.
31	82.90	0.31	0.17	203.
32	84.90	0.11	0.06	72.
33	92.87	0.06	0.03	40.
34	101.90	0.02	0.01	14.
35	104.96	0.05	0.03	31.
36	106.84	0.04	0.02	24.
37	117.87	0.01	0.01	7.
38	119.84	0.02	0.01	10.
39	121.84	0.01	0.00	4.
40	125.87	0.01	0.01	9.
41	127.87	0.01	0.00	6.
42	132.93	0.29	0.16	188.
43	138.87	0.05	0.03	33.
44	140.87	0.02	0.01	12.
45	154.78	0.01	0.01	7.
46	160.90	0.03	0.02	21.
47	162.90	0.02	0.01	10.
48	164.87	0.02	0.01	10.
49	176.90	0.02	0.01	14.
50	178.90	0.03	0.01	17.
51	190.96	0.18	0.10	118.
52	191.93	0.03	0.01	18.
53	192.93	0.25	0.13	162.
54	194.90	0.08	0.04	53.

TABLE 5.4: Results for Mass Spectrometer Run 5.1, for Gas Chromatograph Peak 5

... continued

PEAK NO.	MASS		% RA	% TI	INT
55	199.71		0.03	0.01	16.
56	204.96		0.01	0.01	8.
57	206.93	L	0.13	0.07	88.
58	207.96		0.02	0.01	16.
59	216.93		0.05	0.03	33.
60	248.93	M	0.15	0.08	99.
61	250.93		0.04	0.02	24.
62	266.93	M	0.20	0.11	133.
63	280.96		3.66	2.00	2396.
64	281.96		0.99	0.54	651.
65	282.96	M	0.67	0.37	442.
66	283.93		0.04	0.02	28.
67	284.96		0.02	0.01	13.
68	310.87		0.06	0.03	37.
69	326.84		0.03	0.01	17.
70	340.90	M	0.11	0.06	75.
71	354.96		0.32	0.18	211.
72	355.96	M	0.11	0.06	73.
73	429.03	M	0.11	0.06	73.
74	429.96		0.02	0.01	11.
75	430.96	M	0.06	0.03	40.
76	502.96		0.02	0.01	11.

TABLE 5.4: Results for Mass Spectrometer Run 5.1, for Gas Chromatograph Peak 5

LOW RESOLUTION MASSES SAMPLE RUN: 1368ENG607 SCAN 3
DATE: 07/22/76 TIME: 1715 CALIB. RUN: 0736 RET. TIME: 1:30
SAMPLE: 17-15 BASE M/E: 18 TOTAL IONIZATION: 277950.

INSTRUMENT: CH5 FORMULA: UNKNOWN WEIGHT: 0.000
ANALYST: PYL SUBMITTED BY: BENTRA ACCT. NO.: 109110

REQUESTED RESOLUTION: 1500 THRESHOLD: 4 MINIMUM WIDTH: 1
MEASURED SCAN TIME: 0.0 SEC SAMP. INTVL.: 0.250 MSEC. MINIMUM AREA: 1

10 QUADRATIC DOWN SCANS ACQUIRED
LOW MASS: 10 SCAN TIMES (SECS.) UP: 3.0 TOP: 3.0
HIGH MASS: 900 DOWN: 2010 BOTTOM: 0.0
204 PEAKS READ FROM FILE, 268 PEAKS ASSIGNED CLASSES
72 OF*-2 REFERENCE PEAKS FOUND BETWEEN 18 AND 855 AMU
LIST THRESHOLD = 1.00 % RELATIVE ABUNDANCE

PEAK NO.	MASS	% RA	% TI	INT
5	15.99?	8.94	2.46	6904.
8	16.99?	78.11	21.69	60287.
10	17.99 E	100.00	27.77	77163.
16	27.96	9.93	2.76	7664.
21	31.96	1.48	0.41	1140.
31	42.99	1.81	0.50	1394.
33	43.96 F	2.42	0.67	1870.
51	73.03	4.52	1.25	3488.
62	82.96	1.92	0.53	1484.

TABLE 5.5: Results for Mass Spectrometer Run 10.1, for Gas Chromatograph Peak 10

... continued

PEAK No.	MASS	% RA	% TI	INT
65	84.90	1.33	0.37	1024.
105	132.96	3.04	0.84	2348.
136	190.93	2.82	0.78	2176.
138	192.93	2.75	0.76	2124.
147	206.96	6.87	1.91	5304.
163	248.93	2.76	0.77	2132.
165	250.93	1.39	0.38	1070.
171	264.90 F	1.24	0.34	954.
172	264.99 F	1.55	0.43	1196.
174	266.96	2.22	0.62	1710.
179	280.99	59.78	16.60	46143.
181	281.96	16.58	4.61	12799.
182	282.96	11.53	3.20	8896.
183	283.99	2.86	0.79	2208.
194	354.99	3.16	0.88	2440.

TABLE 5.5: Results for Mass Spectrometer Run 10.1, for Gas Chromatograph Peak 10

Under these conditions it is difficult to go beyond discussion of the types of functional groups and other general structural features of the odor sample.

Complete details of the mass spectrometric analysis are not given here as they followed traditional practice [4, 5, 6, 7]. Analysis of the available MS scans provides some general understanding of the odor sample characteristics.

i. GC peak 4: MS scan 4.1 (Table 5.2) suggests the possibility of sulphur being present as a result of a major peak at m/e = 47 (CH_2SH). According to scan 4.4 (Table 5.3), % RA at 282 is 78.9 and at 284, isotope peak P + 2, it is 13.6. This combination for the intensity of isotope peak to the parent peak is indicative of 4 sulphurs being present in a possible molecular structure of the form $C_{10}H_{18}OS_4$. Since a peak appears at mass 356, it is possible that the species $C_{10}H_{18}OS_4$ is a homolog of $C_{13}H_{24}O_3S_4$, from which an ester group of m/e = 74 has been removed ($CH_2\overset{O}{\overset{\|}{C}}OCH_3+H$).

The presence of chlorine can be deduced from MS scan 4.4 (Table 5.3) by the fact that there is 100% RA at mass 281 and values of 65.5% and 4.4% RA at mass 283 and 285 respectively (2Cl gives RA's of 100, 65.3, 10.6).

ii. GC Peak 5: Analysis of peak 5 indicated that sulphur (m/e = 47, CH_2SH) and ester groups (eg. m/e = 73, CH_2COOCH_3) are present.

iii. GC Peak 10: From scan 10.1 (Table 5.5) it can be seen that an ester compound of mass 355 is present. Peaks at 281, 207 and 133 suggest that these are homologs of the ester compound of mass 355, from which ester groups of mass 74 have been removed.

From the above analysis, it appears that ester compounds, in addition to the sulfur and chlorine containing organics, are the major constituents of the odor sample. Though aldehydes, ketones and acids do not seem to be present in significant amounts, their contribution to the overall odor may, nonetheless, have been significant, since many of them are known to be extremely odorous. Furthermore, some of the low boiling components that appeared as gas chromatographic peak 3 were lost during the subsequent mass spectrometric analysis.

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VI. CONCLUSIONS

The results from this study have revealed both the strengths and weaknesses inherent in a sensory-analytical approach to odor evaluation. Extremely fine gas chromatographic resolutions are required for subsequent identification through mass spectrometry. Since most odors are very complex mixtures this requirement may not be easy to meet. In order to obtain good input to the gas chromatograph, two methods of concentrating odors were investigated. Both gave similar, but not identical results. The degree of resolution was better with the adsorption concentrator, as seen from Figure 6.1. Total identification of odorous components by mass spectrometry was not possible, possibly due to insufficient chromatographic resolutions. Therefore, only tentative conclusions regarding odor composition could be deduced.

It would seem that direct GC/MS interfacing is essential if better identification is to be achieved. The extreme sophistication needed for analysis, as well as the care that must be exercised in interpreting results, makes it appear that routine application of the sensory-analytical technique is not too practical for regulatory use at the present time.

Paradoxically, the strength of the sensory-analytical technique is also well demonstrated by the information that has been obtained during this investigation. Despite the

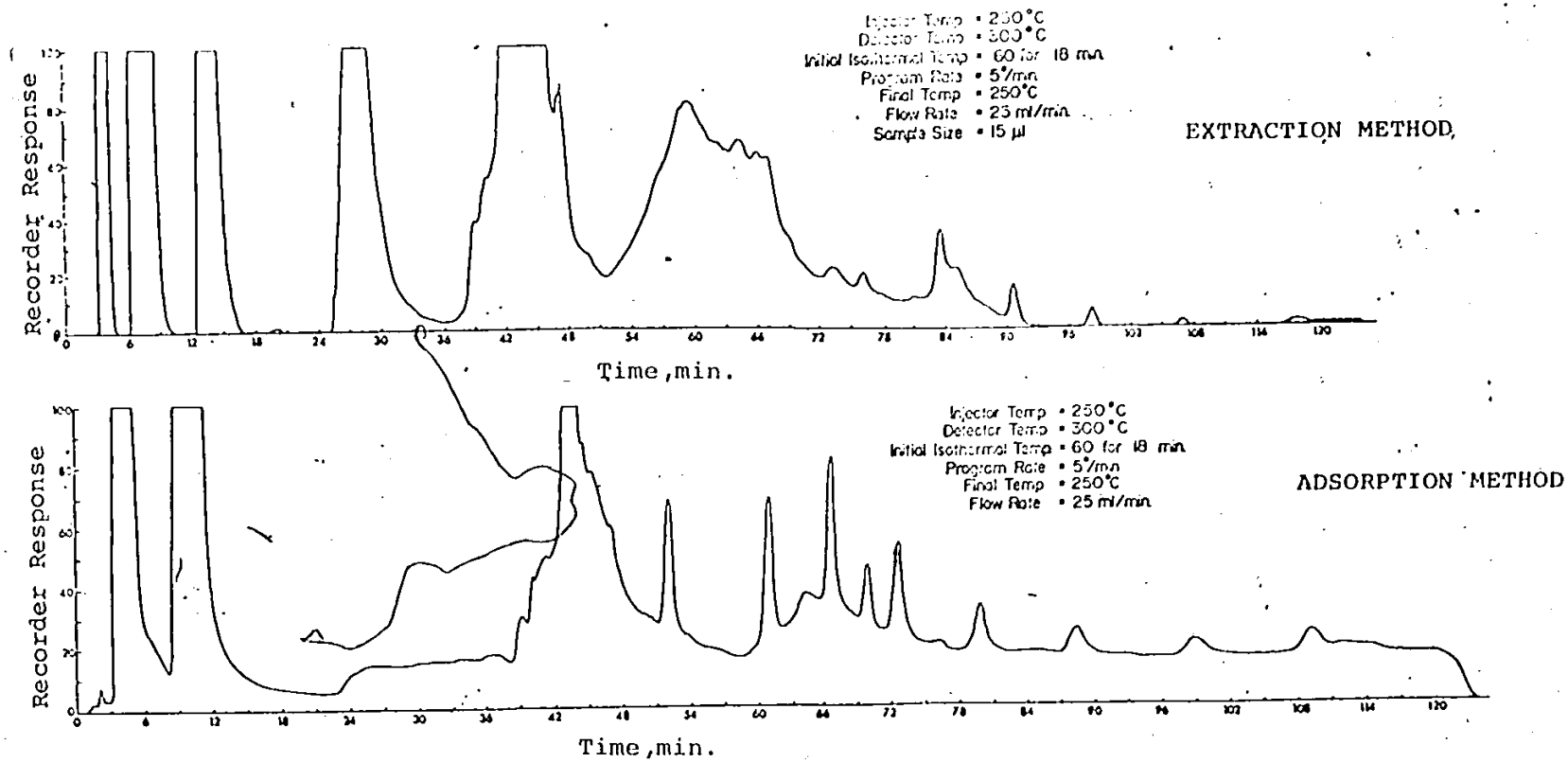

FIGURE 6.1: Comparison of Gas Chromatographic Results Using Extraction and Adsorption Concentration Procedures

tentative nature of the results, their value is undeniable. It is believed that the results of present analysis could not have been anticipated by anyone on an a priori basis. The surprising identification of sulfur and chlorine, for example, seemed for a while to be unexplainable. However, some explanation for the presence of sulfur did emerge from a consideration of the total life cycle of the grain used in the fermentation process. During the storage of the grain, a number of chemicals are used as insecticides and pesticides. Some typical commercial products approved for use in the Canadian grain industry are shown in Table 6.1. In view of the amounts of sulfur involved, it is quite possible that the odorous constituents contain this element as a result of processes originating from the earlier phase of the cycle. The presence of chlorinated compounds may also be attributed either to the pesticides and insecticides or even to the chlorinated city water used for the fermentation process. Another surprising result is the apparent absence of nitrogeneous compounds. The absence of aromatics but the presence of esters is consistent with the chemistry of the fermentation process.

Since it is quite evident that the adsorption technique used to concentrate or collect the sample is more efficient than extraction, it would seem that the best system for trace odorous analysis would involve a concentrator followed by a GC/MS interface. During analysis of any odorous sample the following factors should be considered:

Fumigant	Composition	Application
Kemfume Bin	CS_2 16.4% CCl_4 83.6%	3-4 gallons for 1000 bushels of grain stored in sealed bins
Kemfume Mill Machine	CCl_4 57% $C_2H_2Cl_2$ 20.4% $C_2H_2Br_2$ 19.6%	6% at 21°C on equipment
Kemfume 59 Spot	CCl_4 32% $C_2H_2Cl_2$ 9% $C_2H_2Br_2$ 59%	

TABLE 6.1: Typical Fumigants for Grain Storage Facilities [1]

i. selection of adsorbent: there is no single adsorbent capable of collecting all the compounds from a very complex mixture. Also there will generally be some losses in the concentrate because quantitative desorption of adsorbed species is not always possible.

ii. selection of gas chromatographic column: as mentioned earlier very fine resolution is required in a gas chromatograph column. This is generally achieved by using a very long capillary tube at the expense of high pressure drops.

iii. GC/MS interfacing: some loss of odorous materials can occur during the removal of the carrier gas at the interface of the GC/MS system.

It is evident that a complete identification of all the components in an odorous sample cannot be guaranteed even with the most sophisticated analytical equipment. However, it should always be possible to obtain practically useful information by analyzing odorous mixtures using a concentrator and GC/MS interfacing.

Because complete identification of odorous constituents is seen to require much effort and expense, the potential of sensory analytical methods for providing some appreciation of

odorous samples short of total analysis was also examined in this work. Stack gas emissions from two distillery sources were concentrated using the adsorption technique for analysis by gas chromatography. The purpose was to compare stack emission characteristics with chromatograms from the syrup in order to examine possible correlations between them. Stack samples were collected by passing the gases through an adsorbent bed containing Apiezon L until an odor was detected at the collector exit.

Figure 6.2 compares the grain syrup chromatogram to a chromatogram obtained from a stack gas collected from the Hiram Walker flash dryer. A 1:1 correspondence is discernible for a majority of the peaks. Several new peaks appear, as would be expected, in the stack gas sample since the syrup undergoes flash drying at high temperatures. Under such conditions, some of the esters detected in the syrup odor samples would be expected to break down to lower boiling aldehydes, ketones and fatty acids. Such behavior is apparent from the large number of compounds in the 0-50 minute retention time range in Figure 6.2.

Figure 6.3 compares the chromatograms of stack gas emission from the Calvert and Hiram Walker distilleries. Although it is apparent that the sample collected from the Calvert process was perhaps not concentrated sufficiently, it can be seen that there are high boiling components in both stack emissions. The peaks marked A, B, C and D in the

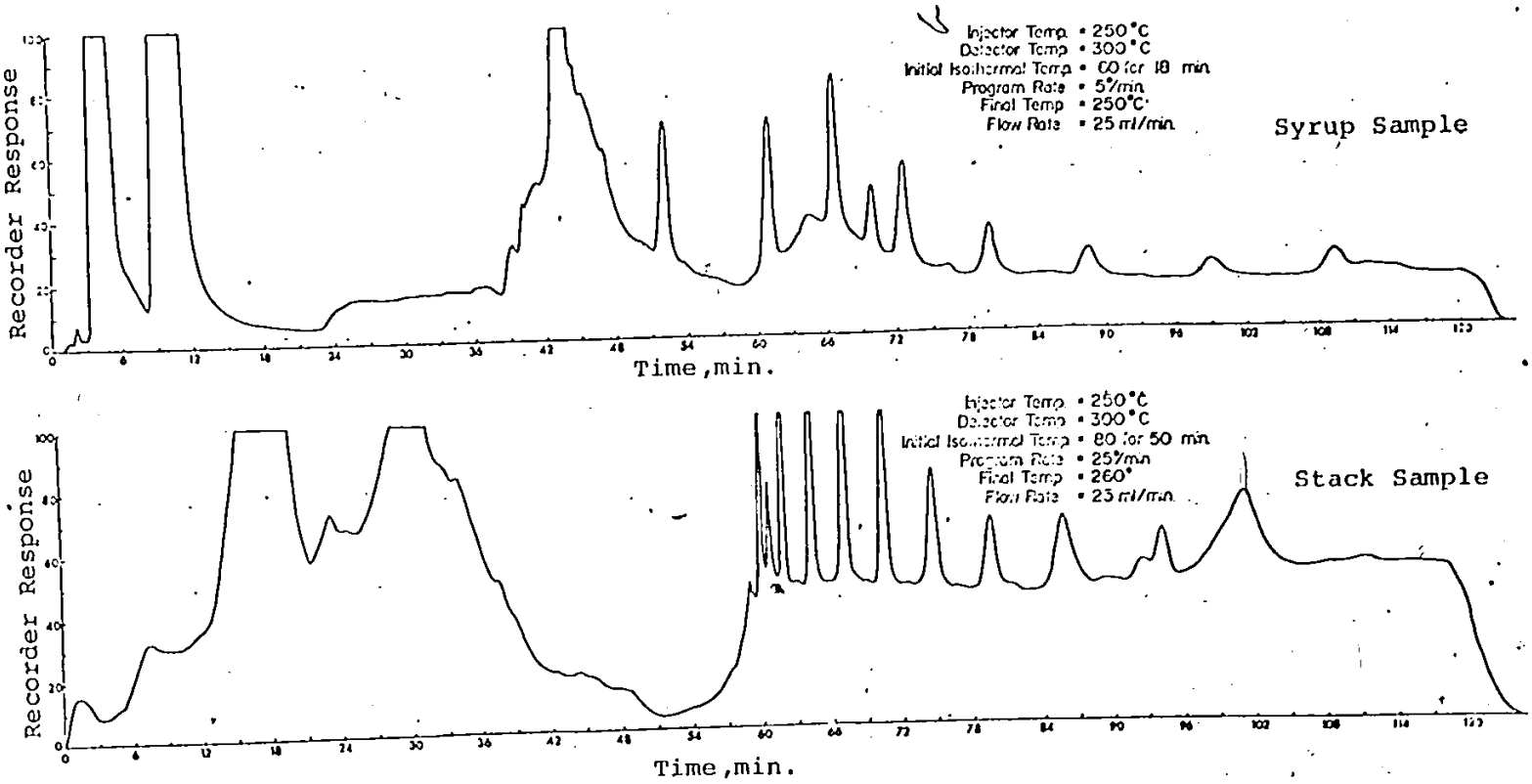

FIGURE 6.2: Comparison of GC Results of Odorous Sample to Hiram Walker Flash Dryer Sample Using Adsorption.

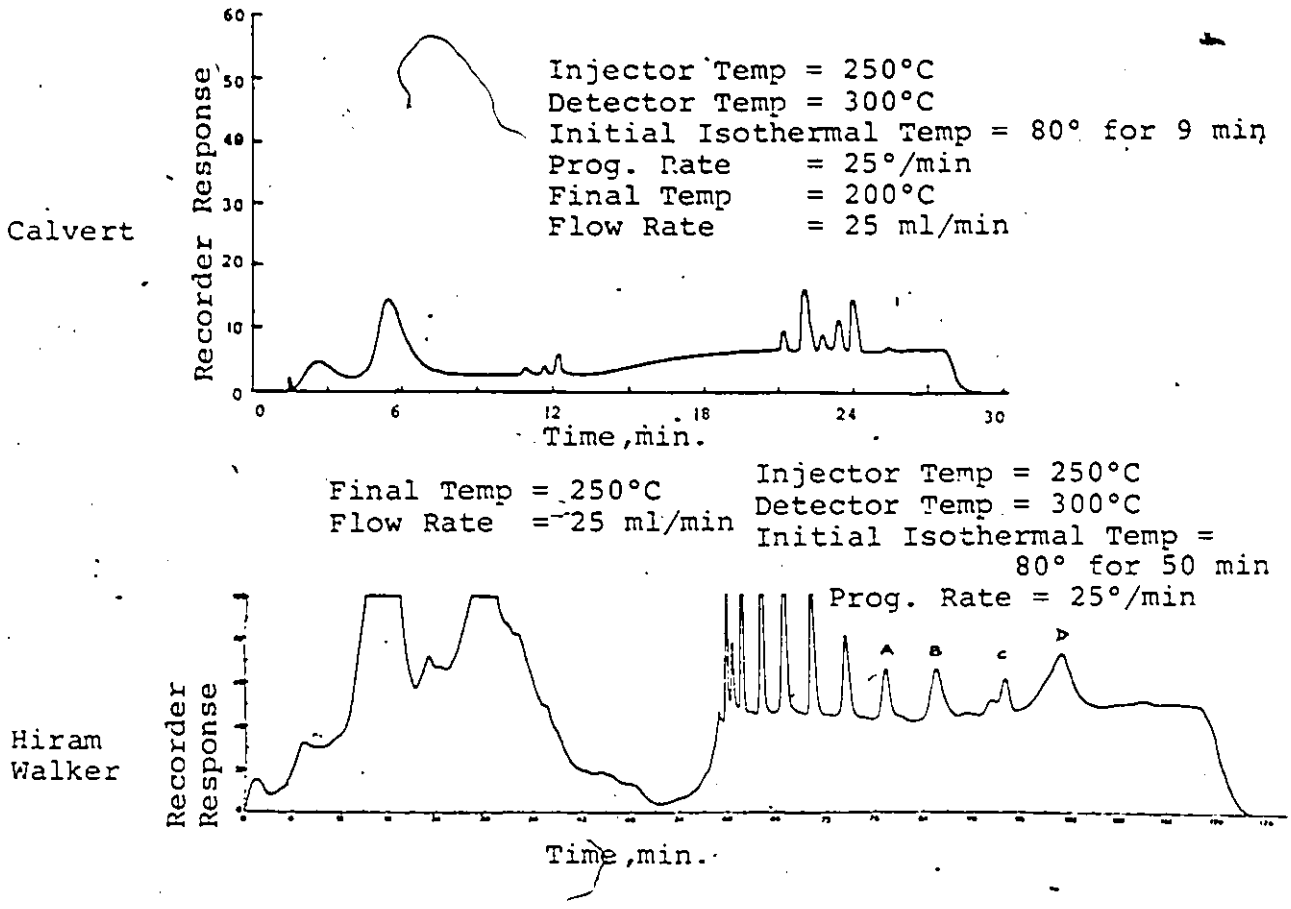

FIGURE 6.3: Comparison of Gas Chromatograph Results of Stack Gas Emission from Calvert and Hiram Walker Dryers using Adsorption Technique

Hiram Walker sample had a burnt type smell. These are missing in the Calvert chromatogram. This difference can be explained in terms of the Calvert drying process which uses a cylindrical rotary shell dryer in which the heating elements are steam jackets. The Hiram Walker system uses direct-fired cocurrent flash dryers. The spent grain is fed to the lower end of the dryer where some burning of the grain is possible. The generation of new compounds could be responsible for peaks A, B, C and D in the Hiram Walker chromatogram.

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