

## **The Control of Product and Package Quality with the Electronic Nose**

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### **ABSTRACT**

A new analytical instrument has been developed over the past several years which can sample odors and develop a “fingerprint” of the odor. This instrument grew out of the work at University of Warwick in the UK, where it was found that phospholipids would absorb odor compounds and change their resistivity. Today’s instrument is based on several different types of sensors, and the instrument has been applied to many types of problems, particularly in the food industry. Through discussions in the media, this instrument has become to be known as the “electronic nose or e-nose”, which is a misnomer.

This paper will discuss the sensor technology, instrument designs, applications of the instrument to packaging problems, and how to design experiments to properly evaluate the instrument for your own applications.

### **INTRODUCTION**

Taste and odor contamination from packaging materials, and package/product interactions involving scalping or other flavor system modification can be a serious issue to a Packaging Engineer. The influence of off-odors or flavors on consumers has become more than quality issue with the increased awareness of the public of food safety problems. Many articles have been written on the subject, and many improvements in packaging materials and in our understanding of the product/package interactions have occurred in the past several years. Currently these problems are most often solved through trained taste panels and/or the use of GC headspace techniques plus instruments allowing the study of absorption/desorption of flavor compounds. Problems with this type of approach is that the individual components found with GC or GC/MS do not necessarily represent the combined sensory effect. Trained panels are not always available to do the sensory work.

Instruments that mimic the human olfactory system have not yet been developed. However, work at the University of Warwick in the UK has resulted in sensor development that, when used in an array, approach the responses of the human system. The instrument has received the nickname of electronic nose or e-nose, and the manufacturers of the instrument have called their instrument by these descriptors. The instrument is not a nose in the sense that it completely emulates the human nose, but there are sufficient similarities to cause the name to stick.

To date much of the work with the instrument has been with food products, flavor ingredients, and water(1-5). Only limited applications of the instrument have been done with packaging materials and package/product interaction problems. Very little has been published(5-11) on the application to packaging. This paper will present the basics of the electronic nose instrument, explore some of the sensors technology employed, and discuss some limited applications of the instrument to packaging material problems. Also, guidelines will be laid out for experimental approaches to help the potential user conduct their own experiments.

### **SUMMARY AND CONCLUSIONS**

A new instrument, the electronic nose has been introduced in the past few years, and it is an additional tool in the Packaging Engineer’s arsenal of tools for solving packaging problems. The instrument still requires methods development to correctly solve problems in packaging materials, but the data available to date shows that the instrument is useful. It is not a replacement for GC or GC/MS analysis or for sensory panels, but is adjunct that can reduce the need for more expensive testing.

## INSTRUMENT DESIGNS AND SENSOR TECHNOLOGY

There are three main manufacturers of electronic noses currently, and a few smaller companies in the start-up phase. The main players are Neotronics Scientific, Aromascan, and Alpha MOS. All of the instruments can trace their lineage back to the initial work(13) at the University of Warwick in the UK. However, instruments available today all have different approaches to presenting the sample to the sensors and to the types of sensors employed.

The basic electronic nose has a process of developing a headspace over the sample being tested, some means of presenting the headspace gases to the sensors, and a computer to record the sensors response and analyze the data. It is at this point that the individuality of the manufacturers begins to emerge because there are obviously a myriad of ways to accomplish this task. Each has an argument of why their approach is best. It is not unlike the state of affairs thirty years ago when GC analysis was at its infancy. One must look at the problems they expect to solve with the instrument, the physical chemistry involved with the compounds and materials, and decide which approach is right for your problem, or which is the most versatile.

**Alpha MOS.** The original instruments by Alpha MOS were based on metal oxide sensors, principally tin oxide sensors. The instruments now available are offered with either metal oxide sensors or conducting polymers. The samples are contained in a jar external to the instrument and the headspace gases are equilibrated at either room temperature or some elevated temperature. The headspace gases are then pumped into the sensor array. The array is mounted in a temperature controlled block of low volume. The sensor array is in multiples of six. A valve system allows for either the sampling of the headspace or purging of the sensors with room air. Tubing used to transport the sample is made of Teflon, but is not heated, so that condensation might occur in the tubing. After the response to the sample is recorded, the data may be analyzed by the internal statistical software or by any desired program.

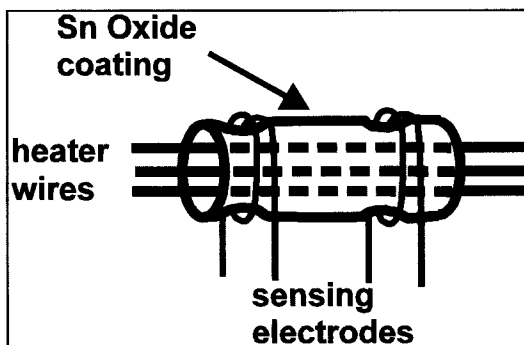
**Aromascan.** Aromascan uses two different approaches to headspace generation. In one method a sample is placed in a non-interacting polymer bag whose headspace is purged with humidified air. The sample is then allowed to equilibrate at either room temperature or an elevated temperature before sampling. One must run a piece of tubing from the sample bag in the oven into the room temperature and then to the sample port. Condensation being one possible confounding factor by this technique. The sensor array is a unit of thirty-two sensors. The instrument uses air passed through molecular sieves as the sensor purging air. Once the data is recorded, one must use the built-in software to analyze the data; no other options are available.

**Neotronics Scientific.** Neotronics first commercial instrument, the E-Nose 4000, was a static headspace instrument using conductive polymer sensors. The sample was placed in a jar in an oven with the sensor head sealed in a chamber above the jar. After the equilibration of the headspace, the sensor array of twelve sensors is inserted into the jar by opening a port in the jar seal. After the sampling time the head rises back into its chamber to be cleaned by dry air. Since no tubing is involved, no condensation problems should exist. Once the response is recorded, the data can be analyzed by any statistical program desired. Neotronics supplies Unistat as the preferred software.

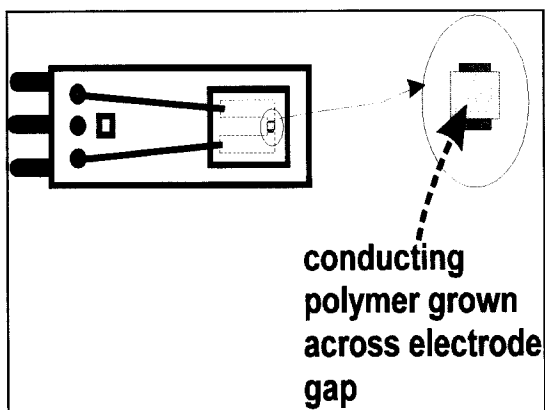
A new Neotronics instrument has been introduced, the E-Nose 5000, which allows the use of a dynamic system and the use of other types of sensors. This instrument can easily be fitted with an auto-sampler for higher through-puts. One can use conductive polymers or metal oxides. There is a provision for additional bays to accommodate other sensory types as they become available. Unfortunately, because of the need to use tubing to transmit samples from the auto-sampler, and from each sensors set, condensation problems could be an issue. Software for analysis is the same as for the E-nose 4000.

## Sensors

**Metal Oxide Sensors.** Metal oxide sensors are made from zinc or tin oxide. These sensors are placed between two electrodes and operated at an elevated temperature -  $\sim 300^{\circ}\text{C}$ . The aroma compound oxidizes on the surface of the sensor and changes its resistance. In their most basic form metal oxide sensors are not very selective in their reaction to aroma compounds, so selectivity is gained by doping the oxide with rare earth metals. The type and amount of dopant controls the selectivity. Metal oxide sensors are deposited in either thick or thin films. Thick films are often printed, whereas thin films are often deposited by vapor deposition. The thin film versions have the highest sensitivity. Reports can be found in the literature of poisoning of metal oxide sensors, but that issue has been overcome for the most part in today's instruments. Metal oxides do offer a sensors that can be used with high temperature sensing applications which is not true of conducting polymers.



**Conducting Polymers.** It was discovered several years ago that polypyrrole, polyaniline, and polythiophene would conduct electricity. The conductivity can be increased by doping the polymers with various ions. As sensors for the electronic nose were being developed, the usefulness of conducting polymers as sensors was explored. If the analyte will adsorb into the polymer it will change its resistivity which can be sensed. Another method that was developed was to coat a simple polypyrrole between the electrodes, and then overcoat it with a functionalized polypyrrole which had some selectivity engineered in to the structure.



Conducting polymers can be coated from a solvent or they can be grown from solution electrochemically. It is through the latter process that the most control over selectivity, sensitivity, and reproducibility can be achieved.

**Quartz Crystals.** Two different types of quartz crystal sensors have been developed. One is based on the sensing of the mass of aroma compound absorbed into a stationary phase coated on the crystal surface by measuring the change in frequency of vibration of the crystal caused by the added mass. These are called "quartz microbalance". Selectivity is achieved by changing the type of coating used. The other type is a surface acoustic wave device. Its method of operation is similar to the quartz microbalance, but in this case one is using a surface or Rayleigh wave to measure the absorbed quantity of material. Neither of these types of sensors are currently being used commercially.

## DISCUSSION

The application of electronic noses has been most often applied to food products and to food ingredients as well as tobacco products. One characterizes the odor profile of products or ingredients that have been judged to be "within specification", or one characterizes the odor profile of materials from various suppliers and that fall within specification. Maps of these data are then created to allow one to make some judgment about how the profiles are grouped. It has been found that the same cultivar of fruit grown in different regions has a different odor profile that is distinguishable by the e-nose.

The manufacturers of these instruments have been, and are currently, working with customers to develop methods of using this instrument with packaging materials to solve package/product interaction problems.

In Europe, Evian screens caps for their water bottles. Much work still remains to be done to customize the instrument to individual problems.

### **Methods Development**

Since the available experience with the electronic noses is rather limited in the field of packaging, methods development will occupy much of your initial development time. One must determine how to sample, how much purge time is necessary for the sensor head and the sample vessel, whether temperature is needed to develop the headspace volatiles, and what type of corroborative data is needed to characterize the samples. The object of methods development is to gain the best data in the least amount of time.

**Sample Preparation.** The usual procedure for sampling is to start by enclosing a sample in some type of container; then flush the headspace of the initial atmosphere; which may contain contaminating aromas from the lab. It is then necessary to allow the aroma profile to re-develop in the headspace before exposing the sensors to the headspace gases. Samples can be heated to assist in the evolution of volatiles. Samples should be protected from the external environment before they are placed in the sample container to prevent contamination or volatile loss. Samples can be of any convenient size, but must be large enough to give a reasonable quantity of headspace volatiles. Typical initial work would be done in a laboratory using static sampling techniques. Once a procedure has been established, dynamic, online sampling can be considered.

**Purging and Equilibration Time.** The only method to determine the best purging and equilibration times for a sample is experimentation. Common sense can be your guide for starting values. If the level of volatiles in the sample is low, as we would hope for most packaging problems, then one should consider a very short initial vessel purge with no intermediate purges on replicate samplings. If the levels are really small, then replicates on a given sample may not be possible, and one must use a fresh sample for each replicate.

Headspace development time, or equilibration time, is needed for all samples. If temperature is used to help generate volatiles, then one must make sure that the vessel is at the same temperature before each sampling. Temperature of the sample must be the same before any measurement to have reproducibility. Instruments are equipped with temperature and humidity probes for the sampling chamber.

**Sampling.** Sampling time is usually set to the maximum of the instrument for the first tests. One can decide from these initial experiments if the sampling time can be reduced. The e-nose sensor responses are plotted against time as the sampling proceeds. One then has a plot like Figure 1. Such plots are recorded for each sample or replicate measured. One can easily see that some sort of statistics must be used to help interpret the data. It is also necessary to decide which time-slice to use for the data. In the case of food and packaging material, it is common to use the response from later times after some sort of equilibrium is achieved. Whatever time-slice is used must remain the same for all samples. For packaging samples, long time slices seem appropriate since it is the long term exposure of the product to the material that is generally the issue.

**Statistical Procedures.** A common way to start the analysis of the data is to determine which sensors are contributing to the data set and which are redundant. One can do this by running a correlation matrix. It is important not to include more sensors in the analysis than are contributing useful information. Too much redundancy, or sensors that are not responsive to the headspace, will only muddle the statistics.

Data analysis can be done graphically, but generally one has difficulty determining the subtleties of the data visually. To reduce the many variables down to a few that can be plotted and more easily understood, multivariate statistics can be used. For initial screening one might use Principal Component Analysis (PCA). PCA is a method of fitting a function to the sensor response values from a given time slice. For example, in Figure 1, the vertical line through the data is at one minute, and one reads the data from each sensor. Similar data at an equal time slice is recorded for each sample or replicate. Once the data is in a matrix, the twelve dimensions of the matrix can be transformed into two or three through PCA. Two or three dimensions can be visualized. If more information is known, such as classification by sample source, one can conduct a Discriminant Analysis to determine the groupings of the data.

**Reproducibility.** As with other types of instrumental analysis, it is also necessary to determine the reproducibility of the sensors response to the aromas. Factors affecting reproducibility are temperature, humidity, concentration of aroma compounds in the headspace, and any carry-over of aroma compounds from one measurement to the next. Temperature is the easiest parameter to control. Most instruments have methods of controlling sample temperature accurately, and the signal is recorded throughout the measurement. Carry-over, the incomplete removal of the compounds adsorbed into the sensor between measurements, can be tested by varying the effect of differing measuring head purge times. Humidity changes, from sample to sample, or within repetitions on the same sample, must be held to a minimum. This topic along with the topic of headspace concentration changes will be discussed further.

Sometimes the aroma effects of a sample, in real life, is dependent on the humidity changing as the sample sensed. In such cases, the change in humidity during measurement will be necessary to reproduce real circumstances. However, the change in humidity must then be reproducible. This may mean that the samples must be conditioned to the same water activity before measuring. Also, replication of tests will require a fresh sample each time. In other cases, such as some testing with paperboard, replications can be made on the same sample if the humidity in the sample vessel is controlled. A procedure for doing this will be discussed subsequently when we discuss paper board measurements.

Changing headspace concentration will affect the sensor response characteristics. A type of sample falling in this category would be a film sample having a very low concentration of off-odor compound in it. Such a sample would not be capable of reproducibly re-equilibrating the sample vessel if one were to try to run duplicate tests on the same sample. Here again, replication of results will require new samples each time.

As one can see from the previous discussion, there is no way to pre-determine the proper laboratory procedure for a sample. The state of knowledge on methods development with the e-nose is similar to that with gas chromatography thirty years ago. Each new problem will require methods development until a sufficient knowledge base is developed.

### **Packaging Examples**

**Paperboard.** The first example of using the e-nose with paper board will show that paper mills produce board with distinctive aromas. This should not be totally unexpected since each mill uses a different recipe for fiber making up the board, and they each tend to use slightly different papermaking chemicals. This combination should result in some differences.

Samples of CCNB were obtained from three different paper mills. Each sample was cut from the reel at the end of the machine and wrapped in aluminum foil to minimize any contamination or loss of aromas. Smaller samples were cut from the board samples using a TAPPI standard Taber sample cutter. This made for easy duplication of sample size. The sample was placed in the jar of the Neotronics E-Nose 4000. Experimentation with purging an equilibration times led to the procedure shown in Table I. It should be noted that the

**Table I - E-Nose Analysis Parameters**

<u>Parameter</u>	<u>Value</u>
Initial Head Purge	5:00 min
Repeat Head Purge	3:00 min
Initial Vessel Purge	1:00 min
Repeat Vessel Purge	0:00 min
Sampling Time	1:30 min
Repetitions per Sample	3

vessel is purged only initially so as not to dry out the board completely. When the analysis of the data was begun, it became immediately apparent that the initial board moistures were different from the three

samples, as shown in Table II. It was a concern that the differences were large enough to affect the results of the test. However, the samples could not be conditioned to the same moisture in the laboratory without the loss of volatiles.

**Table II - Board Equilibrium RH**

<u>MILL</u>	<u>Equilibrium RH</u>
1	30%
2	33%
3	24%

The time slice was taken at one minute, and the data were analyzed by Principal Component Analysis. The PCA plot is shown in Figure 2; the samples from the three mills are sufficiently separated into groups to allow the conclusion that, even with Mill 3 at a significantly different moisture content, there is a difference in the odor profile.

A second experiment with paperboard was carried out on samples provided by a client. The problem was to determine if there was an odor difference from his normal board and an advertised low odor board, and if a new low odor ink lived up to its claims. Also it was planned to see if the procedure could be used to screen samples from the printing process to determine good and bad printing. To determine these facts an experimental plan was developed as shown in Table III. The sensory work was necessary to calibrate the E-Nose results.

**Table III - Experimental Plan**

- control (current board and current inks)
- new board and new ink with regular drying
- new board and new ink with high heat drying
- samples over time to get natural variation of process
- jar testing of samples for sensory input

Needless to say, Murphy stepped in and the samples were not quite according to the plan. There were unprinted samples from the low odor board and from the usual board. Also there were 100% ink coverage samples with the low odor ink, but no control printed samples. Data from the samples was run using the procedure in Table I. The equilibrium moisture in the sample vessel for the two raw board samples was widely separated as shown in Table IV. The Multiple Discriminant Analysis of the data, Figure 3, shows a wide separation regular and low odor board samples whereas the sensory evaluation did not see this difference. A part of the difference was thought to be due to the moisture level differences.

**Table IV  
Equilibrium Moisture Level**

<u>Mill</u>	<u>RH</u>
Regular Board	24%
Low Odor Board	18%

Because the board were from two different mills, and had different moisture contents, a procedure was sought that would eliminate this difference. A procedure of flushing the vessel with air bubbled through a saturated CaCl<sub>2</sub> solution reduced the sensor response to nearly zero. The explanation for this was that the apparently the amount of water vapor was so large that the small amount of aroma compounds were absorbed into the water. It was found that a vial of MgNO<sub>3</sub> solution could be placed in the sample vessel, and at 30C, this would make the headspace RH nearly constant with all of the samples, as shown in Table V. At this RH, the sensors still responded to the headspace aromas. The data from these samples were again analyzed by multiple discriminant statistics, Figure 4. Here the two raw board samples are much closer together and the order of the two printed samples appears to be the same. All of this turned out to be moot since the printed samples were both too odorous for consumer acceptability. However, the differences

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seen by sensory evaluation were confirmed and a potential method for equalizing the sample RH was developed.

**Table V**  
**Equilibrium Moisture Levels with MgNO<sub>3</sub> Solution**

<u>Sample</u>	<u>RH</u>
Regular Board	30%
Low Odor Board	28%
Low Odor Board w/low heat	27%
Low Odor Board w/high heat	28%

### Flexible Packaging Examples

**Laminating Process.** A converter submitted samples of laminations done by three different processes for evaluation. For one of the processes we were given samples run at two different press speeds. Samples, 7-inches by 4-inches were cut and placed in the sample vessel. The instrument parameters were as shown in Table VI. Fresh samples were used for

**Table VI**

<b>Instrument Settings for Laminate Analysis</b>	
<u>Parameter</u>	<u>Value</u>
Temperature	23 C
Head Purge	1.5 min.
Vessel Purge	0 min.
Sampling Time	3.0 min
Replicates	5

the replicates. The data was analyzed by discriminant analysis and is shown in Figure 5. Here we see that each process is represented by a tight grouping of samples that are well separated. In addition, the two press speeds were separated. Therefore additional runs were made with Process 3 at various press speeds and these were analyzed. In addition, the samples were exposed to product an sensory data gathered. In Figure 6, we seen the plot of discriminant scores against press speed for Process 3. The vertical line represents the limit set by the sensory data as t acceptable odor levels. This plot could then be used to allow the E-Nose to help monitor the process for acceptable laminations.

### GUIDELINES FOR SETTING UP EXPERIMENTS

The sample set needed for an electronic nose is not like that which might be submitted to a chromatographer to solve an odor problem. For chromatography, one sends samples of each component of a structure, and perhaps samples of potential trouble components, which are then sampled by the chromatographer. For the e-nose, one needs a series of samples of good and bad samples representing the range of odors found in the normal variation of processing conditions.

A proper set of samples would be those representing a series of known processing conditions, in replicate, along with an independent evaluation of a parameter related to the odor profile, for example, sensory data or analytical data. Using these “knowns” to train the e-nose, one can quickly run samples with lower skilled operators than would be necessary to run headspace GC’s. As has been seen in the previous discussion, the E-Nose can detect differences between samples of packaging materials; and because all of the samples are really identical, one needs enough samples at the various processing conditions to allow statistical processing of the data.

If specific identification of compounds is needed, rather than a quick “fingerprint”, then one should still be using GC or GC/MS to do the analysis.

## REFERENCES

1. Bartlett, P.N., J.E.Elliot, and J.W. Gardner, *Food Technology*, **51** (12):44-48(1997)
2. Hodgins, D., D. Simmonds, *J. of Auto. Chem.*, **17** :179-185 (1995)
3. Hivert, B., M. Hoummandy, P. Mielle, G. Mauvis, J.M. Henrioud, D. Hauden, *Sensors Actuators B*, **24-25**:26-27, 242-245 (1995)
4. Nakamoto, T., A. Fukada, T. Moriizumi, *Sensors and Actuators B*, **24-25**:794-796 (1995)
5. Tan, T., Q.Lucas, L. Moy, J.W. Gardner, P.N.Bartlett, *LC-GC Int.*, **8** (4):218-225 (1995)
6. Holmberg, M., F. Winqvist, I. Lundstrom, J.W. Gardner, E.L. Hines, *Sensors and Actuators B*, **27**:246-249(1995)
7. Pitt, P. (1996) *Packaging Week*, **12** (18), pp.33
8. Anon., (1997) Chemical Application Note 11, Neotronics Scientific Limited
9. Anon., (1997) Packaging Application Note 16, Neotronics Scientific Limited
10. Anon., (1997) Packaging Application Note 17, Neotronics Scientific Limited
11. Anon., (1997) Packaging Application Note 18, Neotronics Scientific Limited



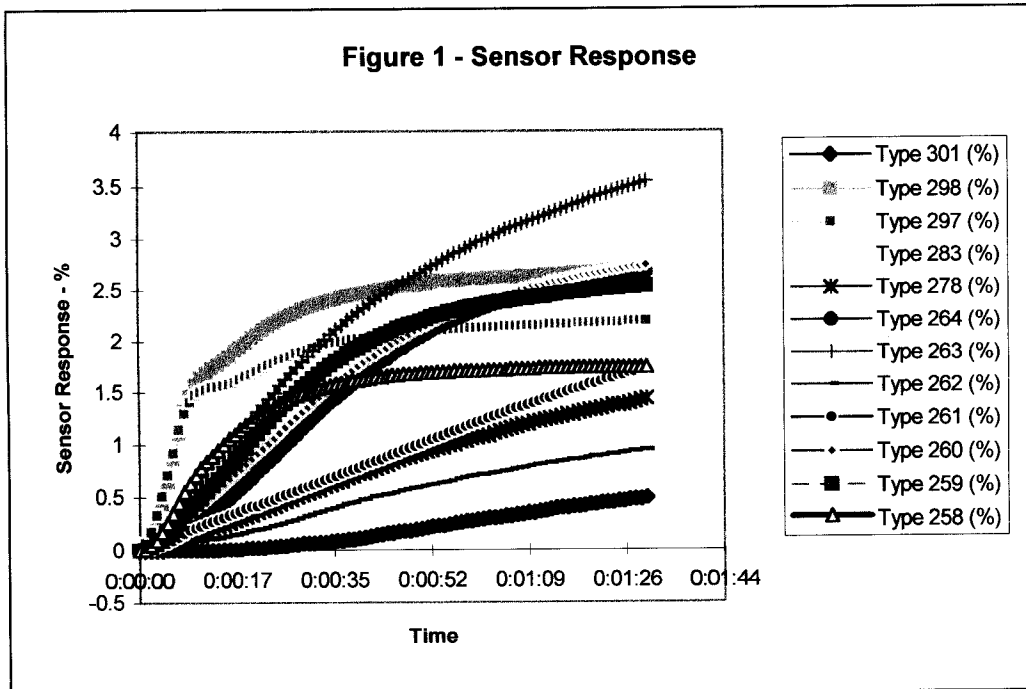


Figure 1 - E-Nose Sensor Response as a Function of Time

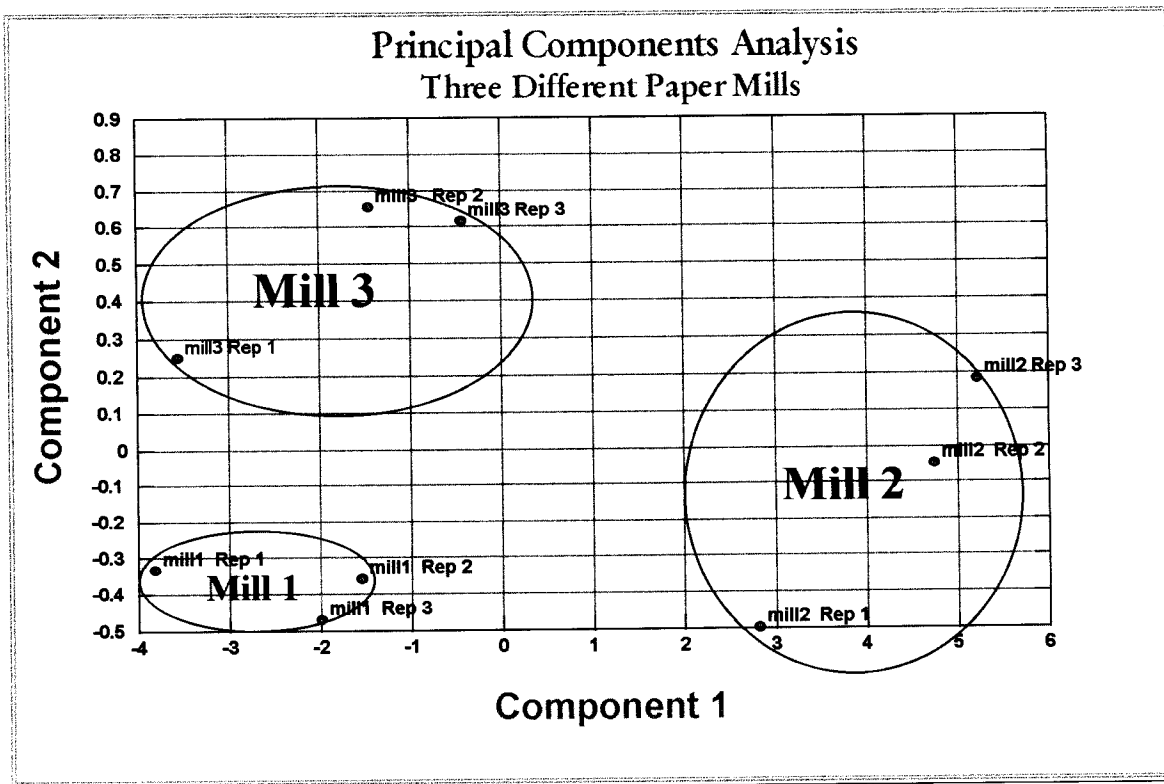


Figure 2 - Principal Component Analysis of Mill Odor Data

**Multiple Discriminant Analysis**  
**Paperboard Data - no humidity control**

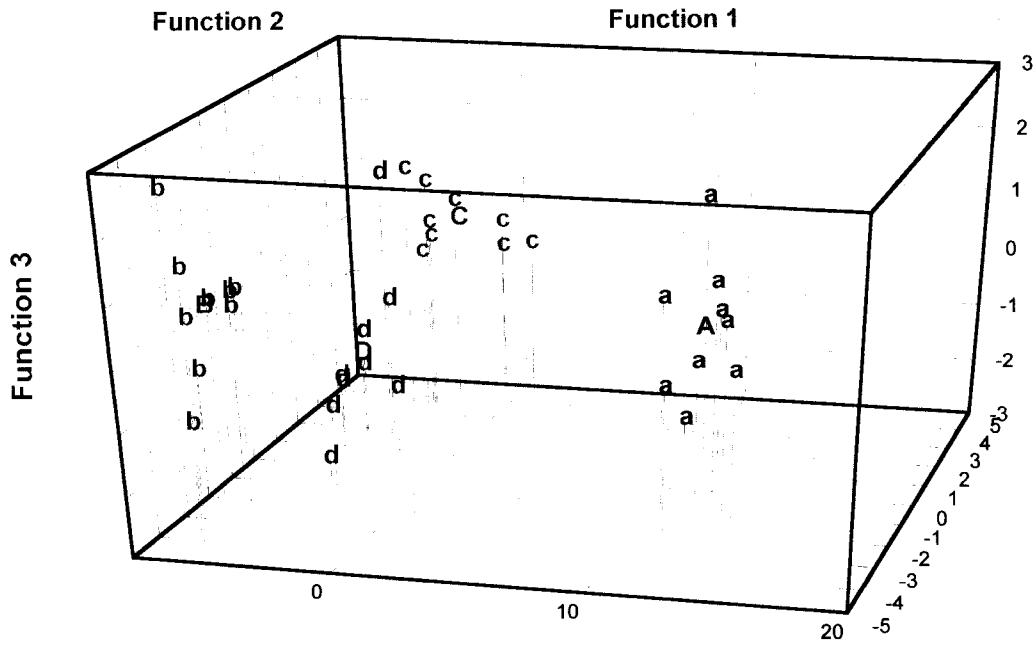


Figure 3 - Multiple Discriminant Analysis of Printing Problem without Humidity Control  
A - Regular Board; B - Low Odor Board; C - Low odor w/low heat; D - Low odor w/high heat

**Multiple Discriminant Analysis**  
**Paperboard - with humidity control**

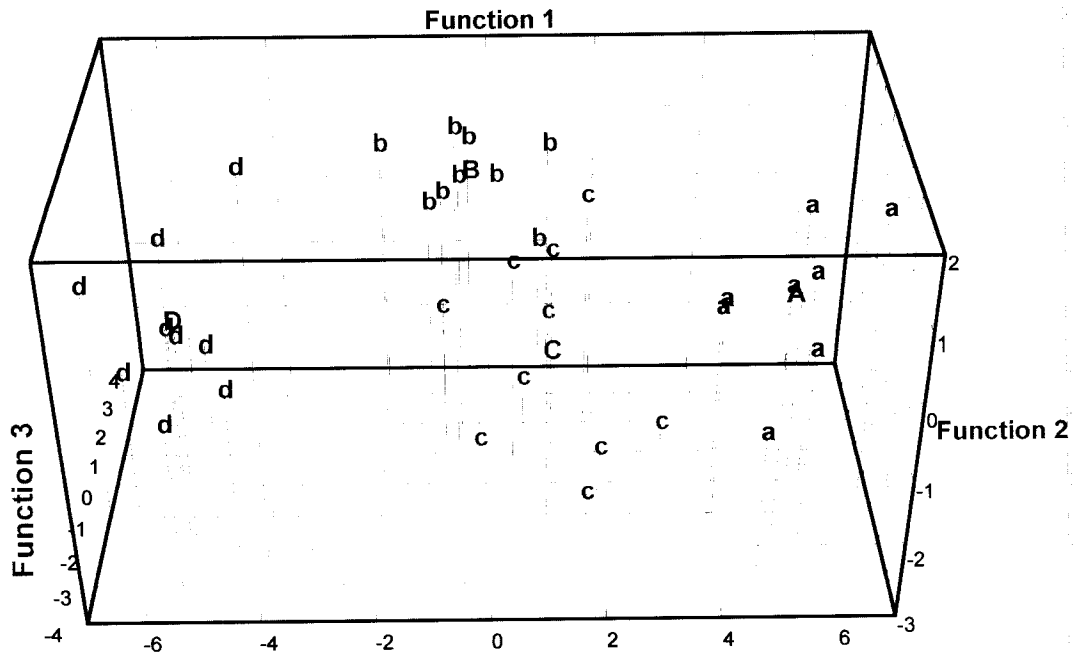


Figure 4 - Multiple Discriminant Analysis of Printing Problem with Humidity Control  
 A - Regular Board; B - Low Odor Board; C - Low odor w/low heat; D - Low odor w/high heat

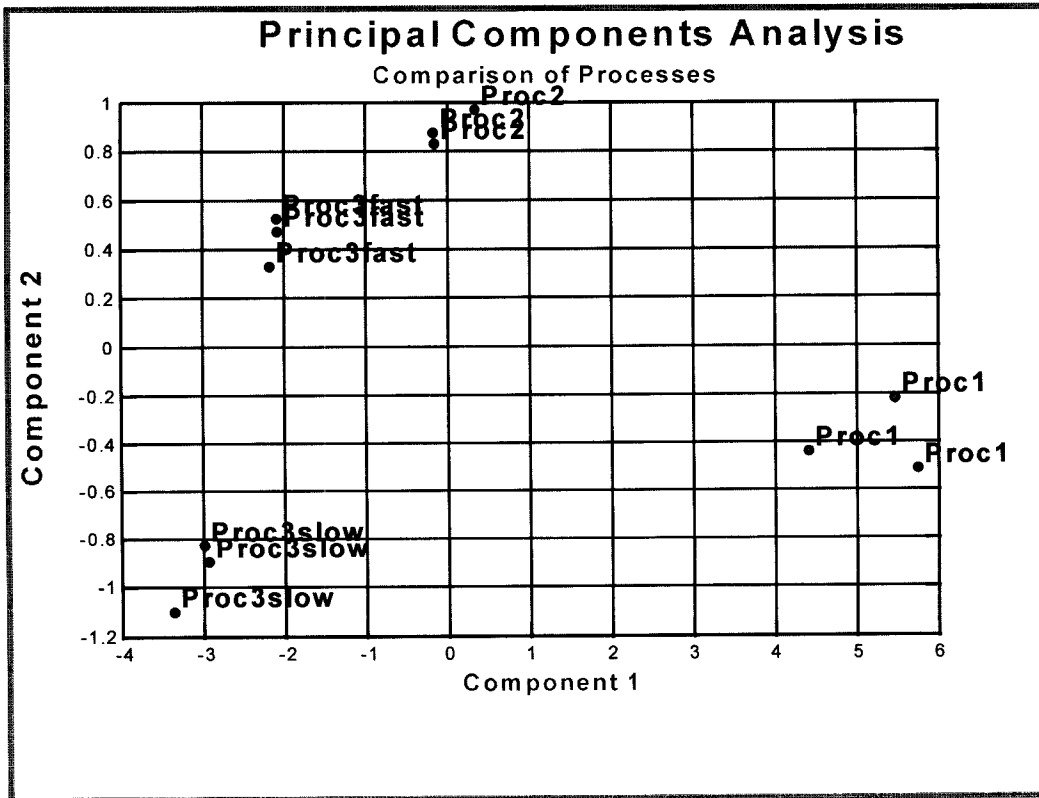


Figure 5 - E-Nose Evaluation of Laminating processes

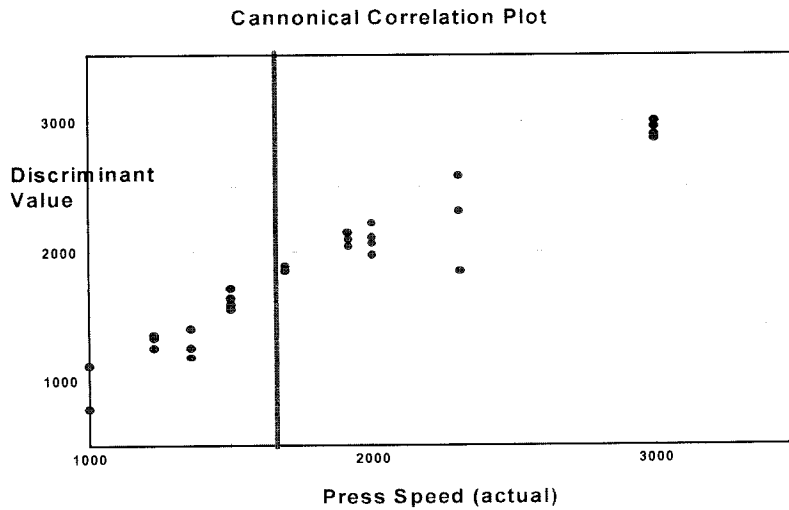


Figure 6- E-Nose Correlation with Press Speed

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