

Quality Assessment of Corn Silage using the zNose®

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Electronic Noses

Conventional electronic noses (eNoses) produce a recognizable response pattern using an array of dissimilar but not specific chemical sensors. Electronic noses have interested developers of neural networks and artificial intelligence algorithms for some time, yet physical sensors have limited performance because of overlapping responses and physical instability. eNoses cannot separate or quantify the chemistry of aromas.

A new type of electronic nose, called the zNose®, is based upon ultra-fast gas chromatography, simulates an almost unlimited number of specific virtual chemical sensors, and produces olfactory images based upon aroma chemistry. The zNose® is able to perform analytical measurements of volatile organic vapors and odors in near real time with part per trillion sensitivity. Separation and quantification of the individual chemicals within an odor is performed in seconds. Using a patented solid-state mass-sensitive detector, picogram sensitivity, universal non-polar selectivity, and electronically variable sensitivity is achieved. An integrated vapor preconcentrator coupled with the electronically variable detector, allow the instrument to measure vapor concentrations spanning 6+ orders of magnitude. A portable zNose™, shown in Figure 1, is a useful tool for assessing the quality of aromatic food products such as corn and wheat silage.



Figure 1- Portable zNose® technology incorporated into a handheld instrument.

How the zNose™ Quantifies the Chemistry of Aromas

A simplified diagram of the zNose™ system shown in Figure 2 consists of two parts. One section uses helium gas, a capillary tube (GC column) and a solid state detector. The other section consists of a heated inlet and pump which samples ambient air. Linking the two sections is a “loop” trap which acts as a preconcentrator when placed in the air section (sample position) and as an injector when placed in the helium section (inject position). Operation is a two step process. Ambient air (aroma) is first sampled and organic vapors collected (preconcentrated) on the trap. After sampling the trap is switched into the helium section where the collected organic compounds are injected into the helium gas. The organic compounds pass through a capillary column with different velocities and thus individual chemicals exit the column at characteristic times. As they exit the column they are detected and quantified by a solid state detector.

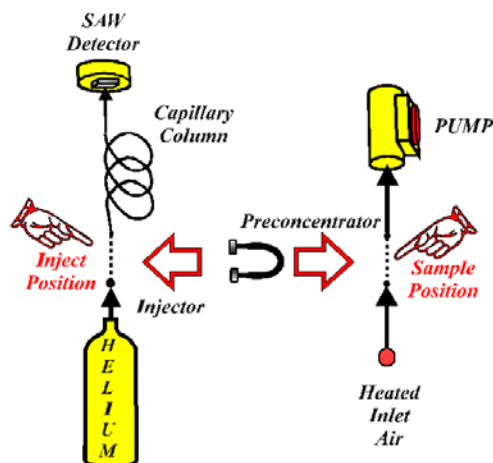


Figure 2- Simplified diagram of the zNose™ showing an air section on the right and a helium section on the left. A loop trap preconcentrates organics from ambient air in the sample position and injects them into the helium section when in the inject position.

An internal high speed gate array microprocessor controls the taking of sensor data which is transferred to a user interface or computer using an RS-232 or USB connection. Aroma chemistry, shown in Figure 3, can be displayed as a sensor spectrum or a polar olfactory image of odor intensity vs retention time. Calibration is accomplished using a single n-alkane vapor standard. A library of retention times of known chemicals indexed to the n-alkane response (Kovats indices) allows for machine independent measurement and compound identification.

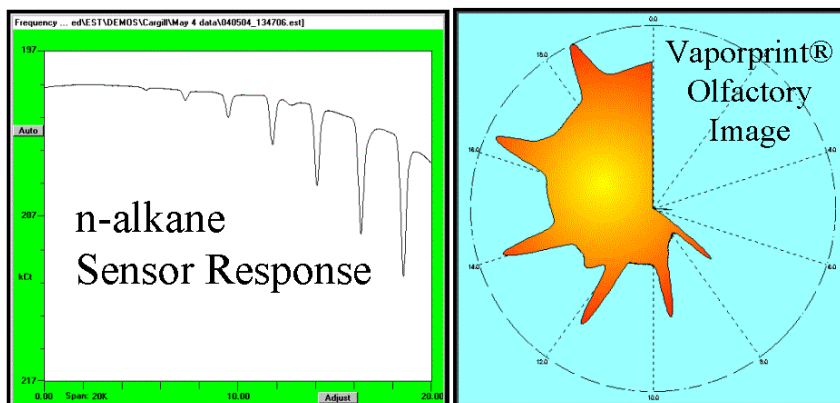


Figure 3- Sensor response to n-alkane vapor standard, here C6-C14, can be displayed as sensor output vs time or its polar equivalent olfactory image.

Chemical Analysis (Chromatography)

The time derivative of the sensor spectrum (Figure 3) yields the spectrum of column flux, commonly referred to as a chromatogram. The chromatogram response (Figure 4) of n-alkane vapors (C6 to C14) provides an accurate measure of retention times. Graphically defined regions shown as red bands calibrate the system and provides a reference time base against which subsequent chemical responses are compared or indexed. As an example, a response midway between C10 and C11 would have a retention time index of 1050.

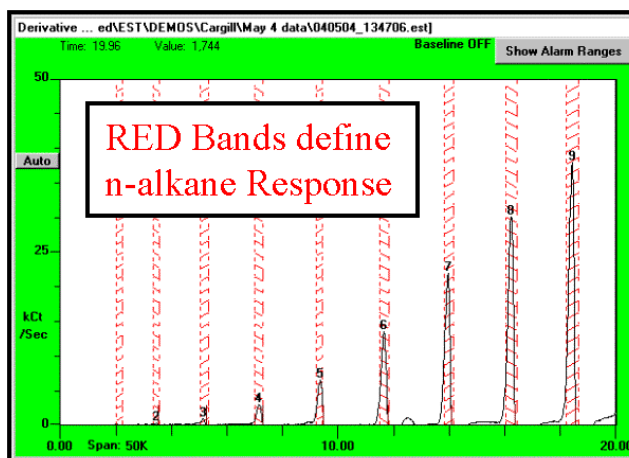


Figure 4= Chromatogram of n-alkane vapors C6 to C14).

Corn Silage Quality

Silage is the storing and partial fermentation of forage plants such as wheat or corn in a silo. For example fodder (livestock feed) is prepared and preserved in an airtight structure that presses the crops. Fermented crops with increased palatability and nutritional value for animals can be stored for extended periods. The primary acid produced by corn fermentation is lactic acid and this compound often gives fermented corn a sour note.



Figure 5- Silage is produced in Silos.

Corn kernels containing any amount of mold (Figure 6) are considered damaged. Moisture allows for the possible growth of molds and toxic substances produced by fungi and mold, such as aflatoxins (aflatoxicosis) and fusarium moniliform (moldy corn disease); both are potentially fatal if ingested. Molds and fungus produce odors which contain microbial volatile organic compounds (MVOC) which are perceived by humans as musty smells.



Figure 6- Moldy corn kernels

Testing Sour Corn Samples

Two different samples (No. 170 and No. 101) of corn kernels judged to be sour were evaluated. The test procedure was to place approximately 5 grams of corn into a 40 mL vial sealed with a septa lid so that headspace vapors would be contained. The vials were thermostated at a temperature of 40°C for 5 minutes before the chemicals within the headspace were measured with a zNose®. Vapors were sampled using a side-ported sampling needle to pierce the septa of each vial.

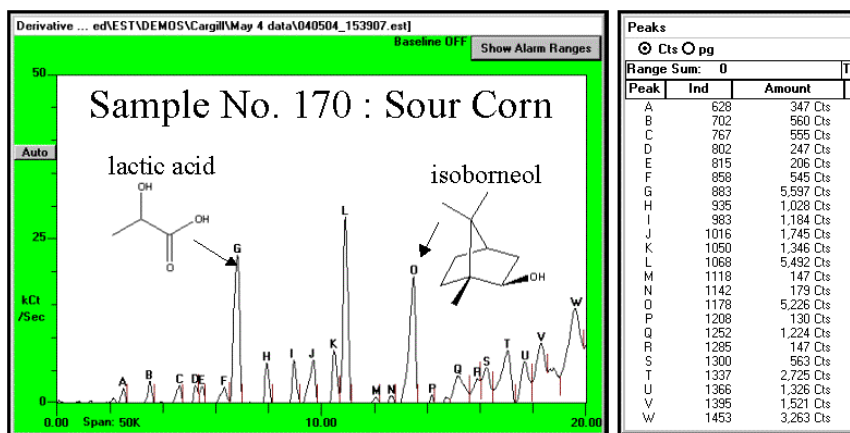


Figure 7- Chromatogram from sour corn sample 170.

Chromatogram results for each of two corn samples are shown together with a tabulation of detected compound indices and concentrations (peak area in counts) in Figures 7 and 8. The vertical scale of Figure 8 is 50,000 counts/second while that of Figure 9 is 20,000 counts/second.

The sour odor from these samples is due to organic acids such as lactic acid shown as peak G in Figure 7 and peak D in Figure 8. Sample 170 had a lactic acid concentration of 5587 counts while sample 101 was considerably less at 2784 counts. Sample 170 also contained two other high concentration compounds at over 5000 counts at indices of 1068 and 1178. The later is believed to be isoborneol which has a musty odor.

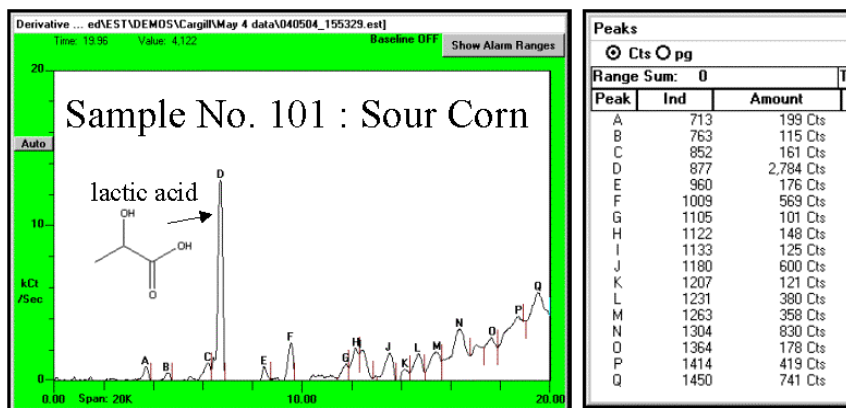


Figure 8- Chromatogram from sour corn sample 101.

Testing Moldy Corn Samples

The headspace vapors from a sample judged to be moldy (no. 150) was tested and found to produce a number of compounds not present in other corn samples and the chromatogram is shown in Figure 9. Compound G which had an index of 1135 is believed to be 3-octanol and had a concentration count of 2992. Compound J (index=1310) had a concentration count of 5482 and is believed to be either indole or undecanal which have pungent odors. Isoborneol, a musty odor, was also present (peak H) but at a much lower concentration count of 294.

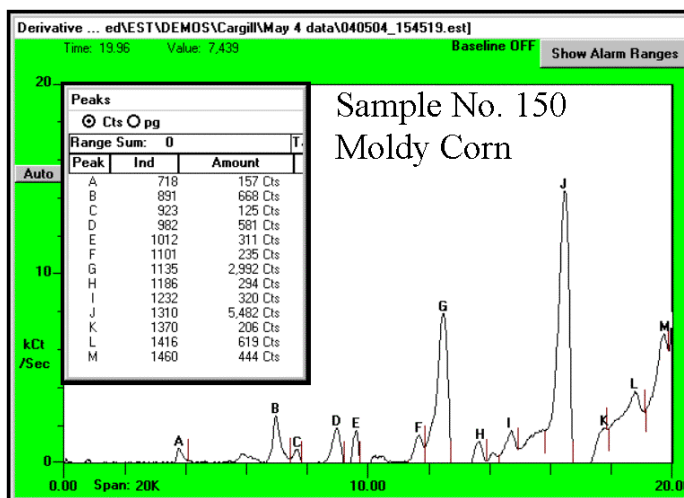


Figure 9- Chromatogram of moldy corn sample No. 150.

Testing Good Corn

Headspace chemistry from two different batches of good corn were tested and found to have only very low concentrations or odor as shown in Figures 10 and 11. Only small traces of lactic acid (468, 205 counts) were detected. Trace amounts of compounds indicative of mold were detected but concentration counts were below 1000 in both samples.

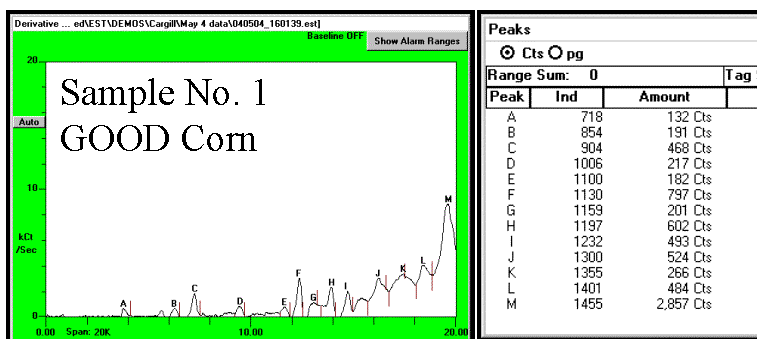


Figure 10- Chromatogram of GOOD corn sample No. 1.

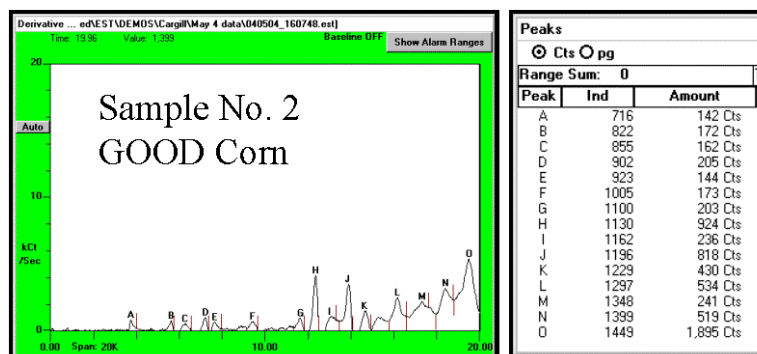


Figure 11- Chromatogram of GOOD corn sample No. 2.

Comparing Corn Odor Chromatograms

Vertically offset chromatograms from all five corn samples tested are shown in Figure 12 for comparison. The lactic acid peak is clearly seen in the SOUR samples and the distinctive compound peaks of MUSTY corn are not present to any large extent in other samples. The relatively odor free chromatograms of both GOOD corn samples are in stark contrast as well.

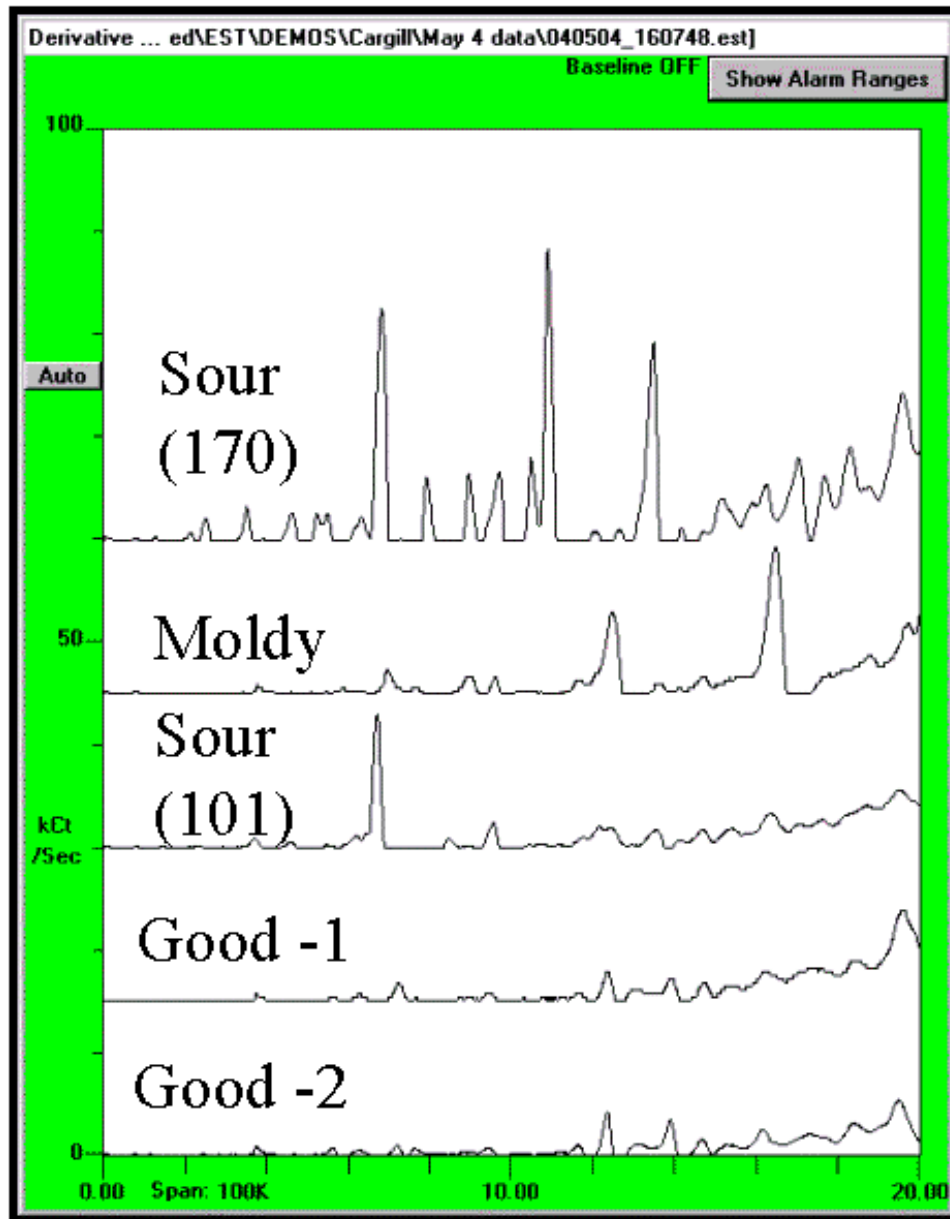


Figure 12- Vertically offset chromatograms from corn samples.

Comparing Corn Odor Olfactory Images

Olfactory images (Vaporprints®) based upon the derivative chromatograms from all five corn samples tested are shown in Figure 13 for comparison. Olfactory images often provide a more user friendly way of comparing odors. The lactic acid peak is easily seen in the SOUR samples and the distinctive compound peaks of MOLDY corn also easily recognized. The relatively odor free chromatograms of both GOOD corn samples give only small images since their odor concentration is low.

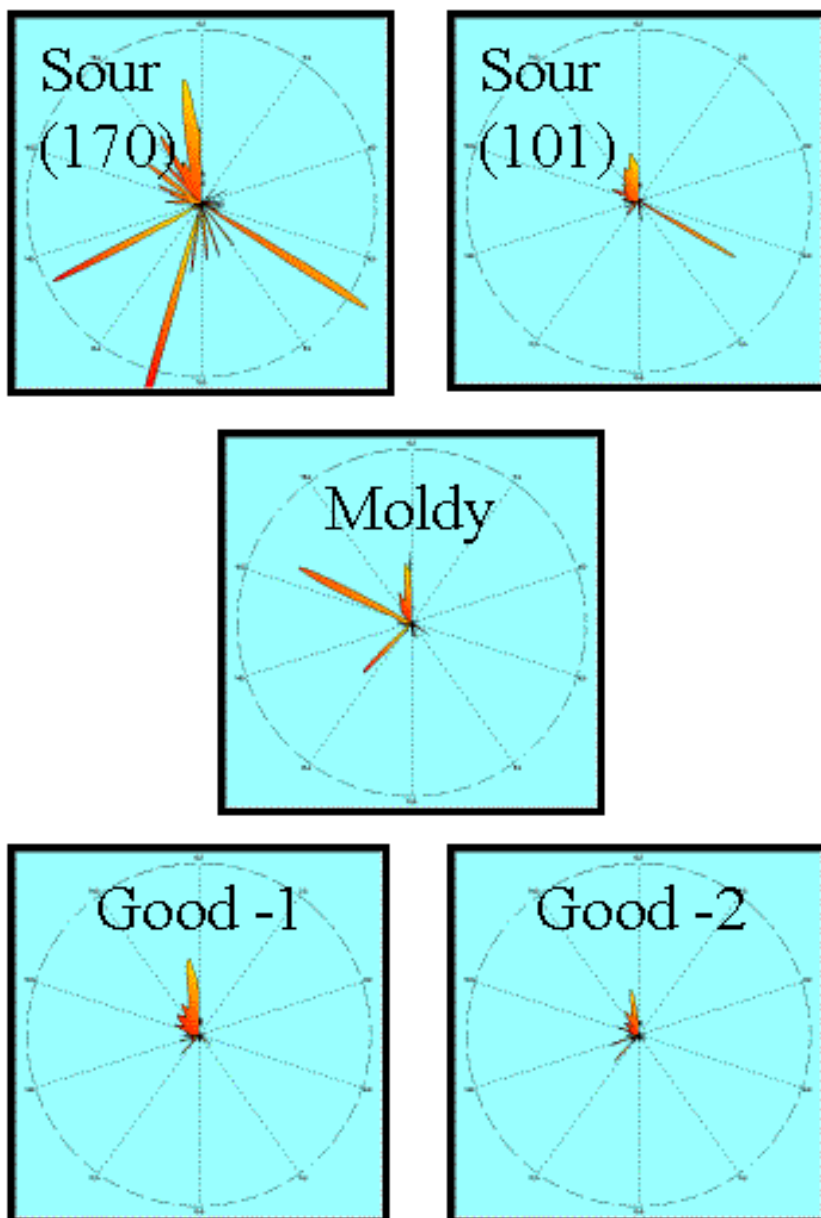


Figure 13- Vaporprint® images based upon corn chromatograms.

Summary

Chemical profiling corn samples judged to be SOUR, MUSTY, and GOOD has shown that it is possible to quantitatively judge quality in a fast and efficient manner based upon the unique chemistry of each odor. Good corn has been shown to produce very little odor and correspondingly low chemical concentrations of target analytes. However, poor quality corn which is either partially fermented or moldy produces odors with relatively high concentrations of target compounds. Indexing of retention times for target compounds using an n-alkane odor standard provides a convenient method of identification and eliminates the complexity of using multiple standards in the field.

Dynamic headspace analysis using ultra-high speed gas chromatography can be coupled with sensory data to affect an objective method of classifying silage such as corn, sorghum, soybeans, and wheat. The chemical and sensory data can be subjected to multivariate analysis such as principal component analysis (PCA) and partial least squares (PLS) methods to determine which volatiles are best used to classify quality. Proper choice of samples and use of optimized variables (compounds indicating off-odors), as well as preprocessing of chemical data, including scaling, transformation, and normalization, may be used to assess quality. Samples with discernable mixed odors, i.e. having musty, sour, smoky, or insect odors can be used together with quantitative chemical analyses. The zNose® provides the speed, portability, precision, and accuracy needed for cost-effective field measurements. Such measurements, because they are based upon well known chromatographic methods, can easily be validated by independent laboratory testing.