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IDENTIFICATION OF FROM CATTLE FEED

CATTLE FEEDLOT OPERATIONS have always been famous for their odor. Owners and operators of feedlots usually become insensitive to the odor or feel that it is not objectionable. But neighbors, especially those downwind, very often do not share this feeling. Complaints which then arise are sometimes translated into legal action to force changes or removal of the feedlot. Reactions to odors are notoriously subjective. Perfumers and food dealers employ persons who are especially skilled in detecting and identifying odors, especially pleasant ones. But on objectionable odors there is far less information, so it was felt that an objective way to measure compounds which cause odors would be helpful in determining the true source of odors. Although the principal interest was in feedlots, other agricultural operations such as dairy farms and horse ranches have similar problems which might also benefit from a broad-base study of the odor problem.

During 1967, 1968 and 1969 a small-scale project on the subject of feedlot odors was conducted in laboratories at the Statewide Air Pollution Research Center, University of California, Riverside. The objective was to identify the odorant compounds from typical feedlot operations and to develop suitable chemical analytical methods for their detection and measurement. The project involved several phases. One part was the sampling problem—that is, determining how to take a sample of air in or near a feedlot operation which is representative, meaningful, and capable of being analyzed for odorous compounds. Since odorants are present in tiny concentrations (a few parts in a billion parts of air) a large volume of air must be treated to selectively extract the odorants for analysis. The second problem was how to analyze such samples to determine the kinds and amounts of those things known to cause odor. The third problem was how to relate such chemical analysis to the odor response of humans.

Little research

Very little research of this kind had been done. Most odor studies were concerned either with the relationship between chemical structure and odor—a study which is useful in the flavor or perfume fields—or with the dilution necessary to destroy an objectionable odor. Very little information has been available on the threshold concentration necessary for odor perception. In the course of this project all three aspects were investigated: sampling procedures for field analysis; analytical methods that might be useful in the laboratory; and a small test apparatus was developed for the evaluation of the concentration necessary to produce an odor response in human subjects. This apparatus produces two streams of air, one of which is first purified and then contaminated with a known concentration of a known odorant. The other stream is a reference which is untreated for comparison (see diagram).

It was logical to direct the first trials toward compounds which were known to be strong odorants. Several classes of compounds were obvious candidates: the amines (generally low molecular weight compounds), sulfur compounds, and low molecular weight organic acids. Sulfur compounds have been used deliberately as odorants for fuel gases for many years. They are added to natural gas as a warning system so that gas leaks will be readily detectable.

Some data published recently by the gas company on odor thresholds for various sulfur compounds is summarized in the table. Note that less than a tenth of one part per billion of tertiary butyl mercaptan can be detected by the human nose. Only a small amount need be added to gas to produce a detectable odor even after substantial dilution of the gas from a leak. The other point which was stressed in this gas company paper was the variability of the test subjects. People do not respond uniformly to odorous compounds. They do not agree either about the nature of the odor from a feedlot; indeed, it is not certain that all feedlots at all times produce the same chemical bouquet of odorants. However, a common odor which many people recognize as a typical animal smell can be obtained from some amines.

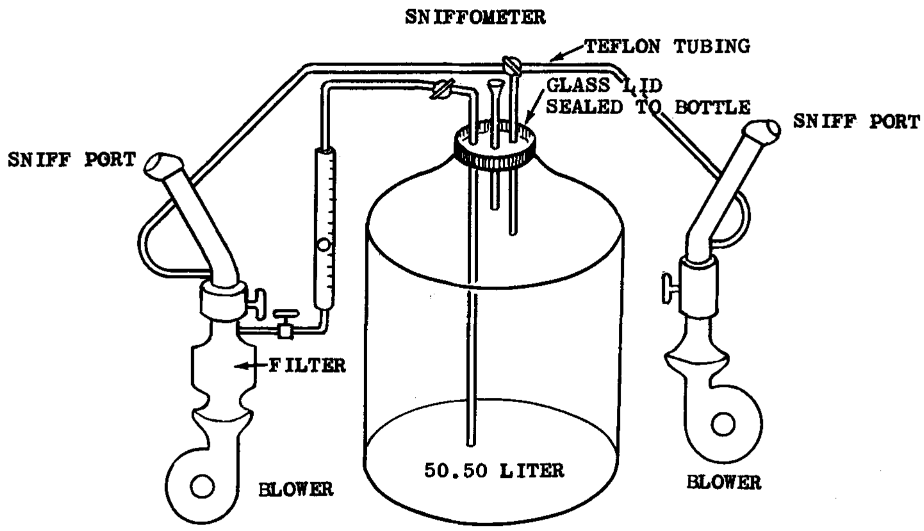
Trimethylamine, especially, is a powerful odorant very reminiscent of feedlot areas. The table shows that about six tenths of one part per billion of trimethylamine is odorous. A study sponsored by the Manufacturing Chemists Association gives a smaller concentration for the threshold (see table).

All of the amines are strongly odorous although none is quite so strong as the trimethyl compound. Ammonia, the parent compound of the amine series, is a much more common substance but it has a much higher odor threshold, several orders of magnitude higher than trimetehylamine. Therefore, while ammonia may be a common decay product from animal wastes it may not make as big a contribution to the odor as some of the lower molecular weight amines, particularly trimethylamine.

Another class of compounds famous for odors are the organic acids. Acetic acid,

ODORS

LOTS



the major ingredient of vinegar, is odorous at about one part per million. Butyric acid, which smells like rancid butter, is detectable at about one part per billion (see table).

First method

The first method of analysis chosen for odorous materials was gas chromatography, primarily because it had been used successfully to identify many air pollutants—particularly those associated with photochemical pollution (hydrocarbons, oxygenated organics, and the peroxyacetyl nitrates). It is a long step from measuring these compounds in a laboratory system containing high concentrations, to collecting samples of ambient air and trying to determine parts per billion traces of them. Nevertheless, gas chromatography was chosen as one of the means of analysis and a method was successfully developed to detect low concentrations.

For this work both flame ionization detectors and electron capture detectors were used. In the latter system it was necessary to convert the amines to a corresponding derivative with a chemical reagent. Another technique which can be used with gas chromatography is to replace the detector on the gas chromatograph with the human nose. This can be very successful, at least for qualitative experiments. The chromatograph is used in a normal way except that the outlet of the column is detached from the detector and led to a place where it can be smelled by an operator. An enormous variety of odors were detected this way in a sample prepared synthetically from a manure mixture.

Perhaps more suitable than gas chromatography in the long run would be some liquid chromatography technique—either paper or thin layer chromatography. Paper chromatography was investigated briefly in the course of the project. In this technique a piece of filter paper is spotted near one corner or one end with the sample to be analyzed; a solvent is then allowed to move along the paper by capillary action. This moves the components of the mixture along the paper until they are separated. Separated spots must then be detected by some auxiliary technique, usually with a chemical reagent. While this is a bit cumbersome compared with direct determination, the equipment required is far more simple than that for gas chromatography and thus might be more suitable for a field operation.

Several techniques

Several other techniques for amines, sulfur compounds, and—to a very limited extent for the organic acids—were investigated briefly. These included infrared spectroscopy, NMR spectroscopy, mass spectrometry, and flame photometry—which others have found useful for the sulfur compounds. One difficulty with the project was the lack of a consistent source of air with the typical odor. Air samples can be taken at any time but the intensity of the odor is quite variable. Freeze traps, bubblers, several other types of other absorbents were all tried as possible sampling devices; none of them were wholly satisfactory. What is needed is a sampler which can be left in a location for several days at least and sampled continuously, preferably with some degree of time resolution. The sample could then be returned to the laboratory and analyzed for the suspected components.

In summary, the project suggested that the most important odorous compounds in feedlot air are the low molecular amines, especially trimethylamine. A contribution from other amines, ammonia and perhaps other compounds cannot be ruled out. Furthermore, it is quite possible that some particular kinds of weather or some special feedlot operations produce a different mix of odorants. There is evidence that decaying feed produces a different odor from the normal feedlot smell. Several of the analytical methods studied showed considerable promise toward a practical means for field study of odors. Perhaps the best of these was paper chromatography but it too requires additional development before it can be a workable tool.

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ODOR THRESHOLD CONCENTRATIONS OF SOME STRONG ODORANTS
(ppm by volume)

	UCR	Ref. 2	Ref. 1
Trimethylamine	0.0006	0.00021	—
Dimethylamine	0.089	0.047	—
Monomethylamine	—	0.021	—
Propylamine	0.009	—	—
Ammonia	3.9	46.8	—
Pyridine	—	0.021	—
Hydrogen sulfide	0.048	0.0047	0.0045
Ethyl mercaptan	—	0.0010	0.0004
T-butyl mercaptan	—	—	0.00009
Acetic acid	—	1.0	—
Butyric acid	—	0.001	—
Formaldehyde	—	1.0	—

Ref. 1. Wilby, F. V. Air Pollution Control Assoc. Jour 19(2): 96 (1969).
Ref. 2. Leonardos, G, endall D. and Bernard, N. Air Pollution Control Assoc. Jour. 19(2): 91 (1969).