

Identification of Malodorous Compounds from a Fish Meal Plant

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Abstract. Odor emissions and control of nuisance odors are important to the agriculture industry because of growing populations around processing operations. Spoilage of fish and associated odors are due to activities of enzymes produced by pseudomonas pathomonas strains. The possibility of removing only those odorants that have long-distance contributions appears to be a more achievable and cost-effective means of controlling downwind odors than addressing all odorous compounds. A research project was conducted at a fish meal plant to identify those specific compounds that contribute significantly to the overall downwind odor. Sampling was conducted using Tedlar® bags, thermal desorption tubes and personal vacuum pumps. The study employed gas chromatography/mass spectrometry-olfactometry (GC/MS-O). The overlaying of chemical analyses results with human panelist data indicated the most offensive odors detected were trimethylamine (TMA) and dimethyl sulfide (DMS). The information was used to successfully design mitigation strategies for reduction of odors downwind of the plant.

Keywords. Multidimensional Gas Chromatography, Odor, Olfactometry, Gas Chromatography, Rendering Facility, Trimethylamine, Dimethyl sulfide.

Introduction

A sound understanding of gaseous emissions from animal processing facilities and their effects requires the expertise of many disciplines. These disciplines may include a broad representation of academia and industry as well as local communities. Agricultural engineers, economists, biologists and chemists will be important in integrating and interpreting the implications of this recalcitrant issue (NRC, 2003). Abatement efforts and mitigation efforts lag behind those in odor detection and monitoring. Credible scientific information on the effectiveness of mitigation technologies on concentrations, rates, and fates of gaseous emissions from animal processing facilities is limited (NRC, 2003). Although there is limited evidence that serious risks to physical health occur downwind of livestock confinement facilities, some research suggests that odor causing substances can cause health effects such as eye, nose and throat irritation, headache and drowsiness; and possibly aggravate allergies, asthma and bronchitis (Odor Control Task Force, 1998). Animal processing industries should anticipate stricter requirements to manage and reduce gaseous air pollutants and odors in their processes in the near future. Air quality standards as a result of the Air Quality Consent Agreement will come from the U.S. Environmental Protection Agency (EPA) in accordance with the federal Clean Air Act (CAA) enacted in 1990. Additional new rules may be set by state or local governments.

Though not well-quantified at this time, volatile organic compounds (VOCs) from animal production operations include organic sulfides, disulfides, aldehydes of 3- through 7-carbon lengths, trimethylamine, C4 amines, quinoline, dimethylpyrazine, short-chained organic acids, and aromatic compounds. The CAA requires that EPA monitor VOCs from industrial operations, which may include some or all livestock operations once the standards are set (Beede, 2006).

Spoilage of fish is principally due to activities of enzymes produced by *pseudomonas pathomonas* strains. Spoilage bacteria critically utilize low molecular weight compounds such as nucleotides and amino acids present in fish muscle. It is the breakdown of these molecules that are responsible for off-odors and other spoilage effects (Herbert *et al.*, 1991). Using gas liquid chromatography, Miller *et al.* (1993) identified some of the principal volatile compounds in spoiling fish as methylmercaptan, dimethylsulfide, hydrogen

sulfide, trimethylamine (TMA), ethylacetate, ammonia and histamine. These compounds are known as volatile bases. Trimethylamine formation is of great interest because it has long been used as a measure of the degree of fish spoilage (Malle *et al.*, 1986). Trimethylamine is produced by the reduction of trimethylamine oxide (TMAO), which is present in appreciable quantities in most marine fish but not in other animals (Hayes, 1995). *Alteromonas* and *A. putrefaciens* are mainly responsible for this conversion. These aerobic bacteria satisfy their oxygen requirements and continue to grow in the depleted oxygen conditions developing in the fish tissues (Horsfall *et al.*, 2005).

Gas chromatography/mass spectrometry-olfactometry (GC/MS-O) has been used to profile the odors of foods and beverages (Friedrich and Acree, 1998; Moio *et al.*, 1993). Multidimensional gas chromatography has been important in qualitatively identifying organic compounds associated with livestock operations with the possibility of quantification of any given sample. Recognizing that olfactometry alone does not provide the scientific information needed to research odor abatement methods, the scientific community is now using additional measurement technologies, such as gas chromatography/mass spectrometry, to quantify accurately the chemical compounds that are present in odor samples (Wright *et al.*, 2004, 2005).

The analysis of ambient samples have included a number of technologies including thermal desorption tubes and Tedlar® bags. Thermal desorption tubes use solid adsorbents for the identification of chemical vapors in the air. This can be accomplished by passing a known volume of air through the tube to quantify the amount of any given compound with an affinity for the adsorbent media (Vahdat *et al.*, 1995).

The objective of this research project was to identify those specific compounds that contribute significantly to the odor downwind of a fish meal plant.

Materials and Methods

Ambient samples were collected 1 km downwind of the fish meal plant and directly from exhaust sources at the plant. Thermal desorption tubes samples were collected at each location for 2, 10, and 60 minute durations. Ambient samples were also collected at selected locations for olfactometry analyses in 10L Tedlar® bags. The bags were constructed with Dupont™ TST20SG4 transparent film, and baked at 100°C for 24 hours prior to sampling per Parker *et al.* (2003).

A GC/MS-O method was developed for this project to allow for detection of low molecular weight compounds to include TMA and DMS. Sorbent tubes were packed with 65 mg of Tenax TA®. Tubes were conditioned at 300°C with a flow rate of 1 ml/minute of Argon. Tubes were sealed in zip top bags and stored for future sampling events. Sampling was conducted with SKC® personal sampling vacuum pumps at a flow rate of 100 ml/minute.

Thermal desorption tubes samples were analyzed using a PAL® autosampler and an Agilent® 6890 GC/mass spectrometer modified with two olfactometry ports (Microanalytics®). The GC was equipped with forte BP5 5% Phenyl / 95% dimethyl polysiloxane 0.53mm ID x 30m and a forte BP20 (polar) Polyethylene Glycol 0.53 mm ID x 25m. Samples were automatically desorbed at 280°C and injected into the GC/MS. The column oven was ramped from 40°C to 240°C at 8°C per minute for a total run time of 38 minutes.

An olfactometry panelist was stationed at each sniff port. Panelists started acquiring data 0.5 minutes after injection of the sample. Data analysis was performed using Aroma Trax® and MSD ChemStation® software. Odor panelist data (aromagram) was overlaid with GC/MS data to produce a chart with representations of relative compound quantities and panelist perceptions of respective compounds (Fig. 2).



Figure 1. Photograph of the GC/MS-O (left) and Panelist Sniffing Sample (right).

Results and Discussion

Our analyses indicated that the most offensive odors in the fish meal plant samples were low molecular weight VOCs. The highest detection of these compounds was achieved when we modified the GC/MS method to qualify these compounds with the mass spectrometer.

Identification of the most odorous compounds and their relative quantities can be seen in Figures 2 and 3. We identified several compounds with hedonic tones of -2 or -3, and they are shown in Figure 2. The character of individual odorants was compared to the overall odor in the Tedlar® bag samples.

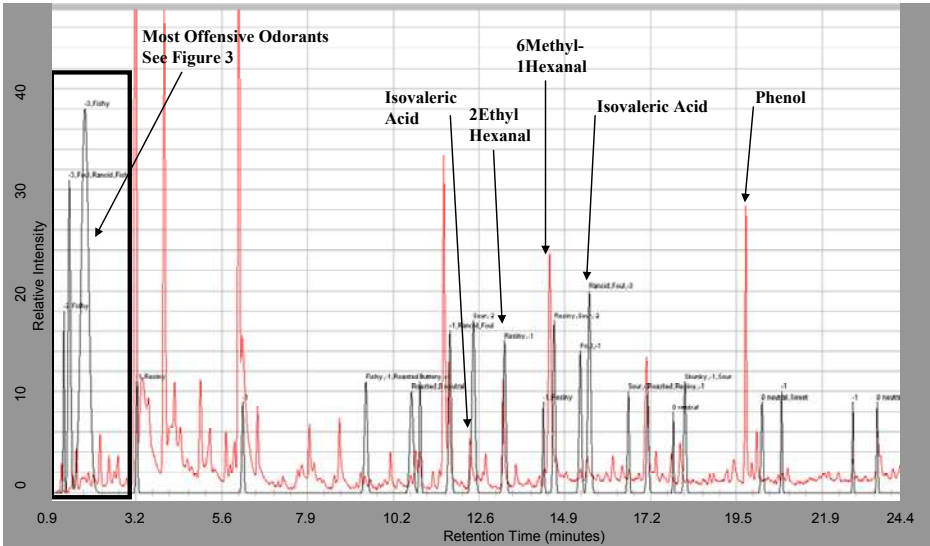


Figure2. Graph showing an overlay of the chromatogram (red) and aromagram (black). Those compounds with the most offensive odors are identified on the graph.

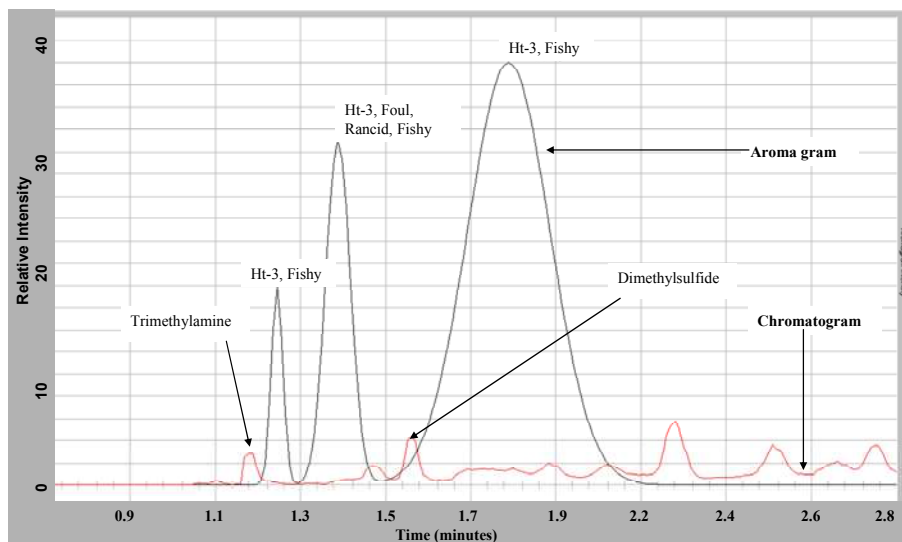


Figure3. Trimethylamine and dimethyl sulfide with corresponding panelist perception including hedonic tone and relative qualifier.

TMA and DMS contributed to the overall nuisance odor, and had the highest panelist perception of odor at ambient concentrations. Fig 3 shows 3 aromagram peaks corresponding to TMA and DMS. The first two peaks are the panelist's perception of TMA. The third peak is the panelist's perception of DMS. The marriage of GC/MS and olfactometry was integral in determining the individual odorants in these samples. Identification of individual odorants moves characterization of nuisance odor to the development of mitigation strategies.

The identification of TMA and DMS in these thermal desorption tube samples and Tedlar® bag samples can be seen as progress. These two compounds can be managed by adjusting existing scrubber technology in this particular plant. TMA has a reasonably low detection and recognition threshold (Table 1) (Van Gemert, 2003).

Table 1. Detection and recognition thresholds for TMA and DMS.		
Compound	Detection Threshold	Recognition Threshold
TMA	0.00026 ppmv	0.0034 ppmv
DMS	4.1 - 33.2 ppmv	730 ppmv

It is typically the offensiveness of the odor that is the true indicator over whether an odor is perceived as a problem. Offensiveness and concentration are not necessarily correlated, the perceived offensiveness of an odor may increase or decrease in response to concentration changes. Analysis of processing facility emissions adds beneficial data needed to understand and mitigate downwind odor.

Conclusion

The objective of this research project was to identify specific compounds that contribute significantly to the odor downwind of a fish meal plant. Identification of TMA and DMS in this study opens up possibilities of mitigation of nuisance odors associated with this fish meal production facility. We are progressing to an understanding of compound fate and transport needed to seriously address nuisance odors associated with a wide variety of agricultural industries.

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