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Method Development for Determination ff Odors as an Indicator of Environment Condition in Tanneries Surroundings

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Abstract

In the state of Rio Grande do Sul there is no specific legislation setting odor limits generated by industrial processes. However, environmental agencies have established in the operating permits that certain activities should be conducted in order not to emit odoriferous substances that may be perceptible beyond the property limits. Odor measurement is highly complex, since it depends on the perception and sensitivity of the evaluator olfactory system and the identification and quantification of the chemicals that give rise to odorous emissions. Acordding to IULTCS 2008, the major sources of odors in the leather tanning process are related to the putrefaction of skins, the release of gases (ammonia and hydrogen sulfide) and the use of volatile organic compounds, as well as odor generated from the effluents treatment and sludge dewatering. Considering the requirements of environmental agencies and people's complaints, the determination and monitoring of odor and an environmental condition indicator is needed. The development of a low cost and simple methodology from an operational point of view to measure and monitor the odor in the vicinity of leather tanning factories meets this need. Therefore, the population perception of odors and the concentration of NH_3 and H_2S gases present in the monitoring points were considered in this research.

Keywords: leather tanning, odor, ammonia, hydrogen sulfide.

1 – Introduction

The activities carried out in a tannery, by the very nature of the production process of leather, are related to several significant environmental impacts. Odor is among the impacts that are most remembered by the population, especially for the communities located near tanneries. As IULTCS 2008, tanneries have several sources of odor generation, being the main ones skin putrefaction, release of ammonia (NH_3) and hydrogen sulfide (H_2S) and use of volatile organic compounds. The generation of odor can also occur during wastewater treatment and sludge dewatering.

With molecular formula H_2S and molecular weight of 34g, the hydrogen sulfide can occur when there is lack of oxygen, in the presence of organic matter and sulfate. Much of the hydrogen sulfide gas in the atmosphere has a natural origin and is present around springs and lakes, also being an air contaminant in geothermally active regions. The hydrogen sulfide is characterized as a colorless gas that is soluble in various liquids, including water, alcohol, ether, glycerol and petrol (Silva 2008).

H_2S is a gas that displays a long list of disadvantages: it is toxic because it combines with the cytochrome iron and other essential compounds which contain iron in the cell; it is an offensive odorant (rotten egg odor, easily released into the atmosphere, being detected by most individuals at extremely low concentrations). It is found in sewage treatment plants, mainly in turbulent flow stages and is extremely corrosive in a moist atmosphere, turning into sulfuric acid and causing a decrease in the amount of dissolved oxygen in the liquid mass - 2 moles O_2/1 mole of H_2S (Leite et al. 2001; Silva 2008).

Ammonia is a colorless gas at room temperature. It has an extremely strong odor and is considerably lighter than air, presenting melting points and boiling -77.7° C and -33.35° C, respectively. It is quite soluble in water (1992 cited Barros Felix; Cardoso 2004). In the atmosphere, ammonia has a residence time ranging between one and two weeks. It has several applications, among which we may highlight its use as a nitrogen source in the production of fertilizers, neutralizing agent in the oil industry and refrigerant in industrial systems (Stuerchler 2002 cited Felix; Cardoso 2004).

A positive fact to be mentioned is that even in ammonia concentrations in the range of tens of ppm, it produces an extremely unpleasant odor, favoring its detection (Stern 1976 cited Felix; Cardoso 2004). The limit value of ammonia a person can be exposed to during 8 hours of daily work without causing health damage is 30 ppm (Stuerchler 2002 cited Felix; Cardoso 2004). The balance between the volatile compounds HNO_3, HCl and NH_3 and the components of the aerosol NH_4NO_3 and NH_4Cl make it difficult to obtain representative and reliable data on measurements of free ammonia in the atmosphere, since, depending on the environmental conditions of sampling, they can be readily volatilized at ambient temperature (Felix; Cardoso 2004).

The unpleasant odor is the form of pollution that most directly impacts the human being, becoming a complex problem when it bothers a reasonable number of people, interfering with their wellbeing (Wark; Warner 1976 quoted in Barros 2007). According to Barrenetxea et al. (2003) quoted in Barros (2007), air pollution can be understood as air pollution by insertion or temporary presence of materials unrelated to its natural composition, or in a higher than natural rate, in the states of matter aggregation, or even in the form of radiation.

The word odor is almost always used as a synonym for unpleasant smell, but that term is defined by science as the result of the presence of volatile and semi-volatile substances assimilated by the human olfactory system (Godish 2004 cited Barros 2007).

Basically, for a substance to be odorant three conditions must be given: being volatile; being able to be absorbed by the human sensory apparatus and being a cause for changes in olfactory perception (Wark; Warner 1976 cited Barros 2007).

Odors can originate from natural and anthropic sources, with examples of natural sources such as volcanoes, aquatic environments and changes in the biogeochemical cycle of Earth. In natural environments, aquatic microorganisms, such as bacteria, fungi, actinomycetes, cyanobacteria and eukaryotic algae are, in most cases, responsible for the odor-causing compounds. In turn, the major anthropic sources that cause odors are the industries and sewage treatment plants (Canela 1999).

1.1. Odor Classification

According to Balbinot (2010), odorous compounds may be classified into three classes: sulphurous, nitrogenous and oxygenated or aromatic, as shown in Table 1.

Table 1 - Odorous compounds and odor characteristics

Class	Description	Odor characteristics
Sulphurous	The sulfur compounds are among the most odorous substances known and can be detected at very low concentrations, at levels of ppb. Regarding the chemical structure, they fall into two categories: sulfides (-S) and mercaptans (-SH). The appearance of volatile organic sulfur compounds associated with the presence of microregions with anaerobic activity, resulting in fermentation of the sulfur compounds present and/or breakdown of molecules through thermal heating.	Rotten eggs, strong and irritating, strong garlic, strong possum, ocher.
Nitrogenous	The main odorous nitrogenous compound found in industrial processes is ammonia (NH_3). It is produced by the anaerobic and/or aerobic decomposition of proteins and amino acids.	Spicy and irritating, putrefying fish, ammoniacal, putrefying meat, fecal, nauseating, deteriorating.
Oxygenated or Aromatic	Substances originated from the decomposition of organic matter. Volatile fatty acids such as acetic acid and butyric acid are derived from oils and greases. In turn, aldehydes and aromatic compounds come from the decomposition of woody debris.	Vinegar, butter, sweat, ocher, suffocating, fruity odor, rancid and penetrating, alcohol odor, sweet odor, mild odor.

Source: Adapted from Balbinot (2010).

1.2. Characteristics of odors

According to Vieira (2013), the sensation caused by the perception of an odor can be considered under certain dimensions such as character and hedonicity described below:

1.2.1. Character of an odor

The character (or quality) odorant describes in words what the odor is like, using a reference vocabulary for taste, odor description and sense of smell (Vieira 2013). The concepts are very subjective as the olfactory sensation it is individualized, although the types of responses are generally analogous to a homogeneous population (Fernandez 1997; Schirmer 2004 cited Schiermer et al, 2008). Determine the quality of the odor becomes very complex task, because to translate the odor perceived looks is influenced by the person's repertoire (Schiermer et al. 2008). Among the most common forms of representation of odor is smells wheel (Figure 1), where eight categories are highlighted (families) of easily recognizable odors: floral, vegetables, fruity, medicinal, chemical, offensive, earthy and fish.

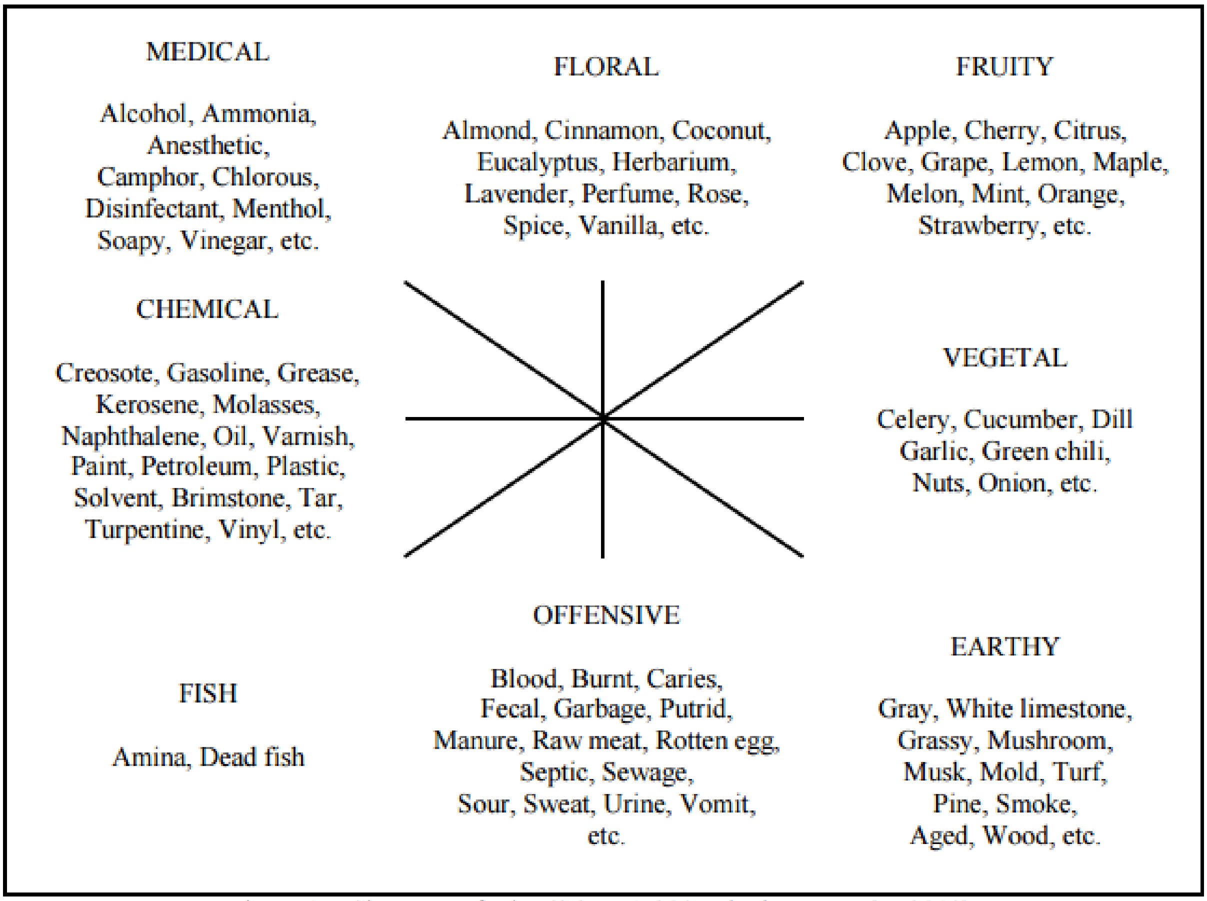

Figure 1 – Character of odor (SOUZA 2007 cited BILBINOT 2010).

1.2.2. Hedonicity

The hedonicity of odor can be defined as the feature of the substances present in the atmosphere of causing pleasant or unpleasant sensations, tolerable or intolerable to the human olfactory system. According to Vieira (2013) assigning a value to the hedonic tone of an odor by an individual is "subjective", a fact owing to the personal experiences and memories of the evaluator that include their feelings and values in the process of decision making.

1.3. Legislation

There is no legislation in Brazil establishing quantitative limits for the emission of odor. In the case of the State of Rio Grande do Sul, the limits set forth in the environmental licensing of industrial activities must be established by the Government (State Law Nº 11520/2000), which bans the emission of odoriferous substances that may be perceptible outside the property boundaries.

1.4. Odor measurement methods

The measurement of odors can be performed using analytical methods that inform the chemical composition and concentration of the compounds responsible for the odor; sensory methods that provide the nasal perception of odor; and sense-instrumental methods that are capable of determining the concentration of an odorant compound or a mixture of odorant compounds in real time (Romain; Delva; Nicolas 2008; Zarra et al., 2010 cited Vieira 2013).

According to Brattoli et al. (2011), sensory measurements can employ the human nose as the odor detector, being directly related to odor properties perceived by the receptors. Sensory measurements may involve two techniques:

1. Quantitative, by using device associated to human olfaction.
2. Measurements of olfaction only, where there is no use of equipment.

Even if one has knowledge and detection of compounds responsible for the odor, according to Vieira in 2013, the perception of odor is subjective and cannot be directly related to chemical concentrations.

Whereas there are still many gaps for the assertive detection of odors to relate quantitative values associated with the perception of this odor, and that there is no specific methodology for measuring odors, this study aimed to develop a low-cost, simple methodology from the operational point of view, for measuring and monitoring odor in the vicinity of tanneries. Therefore, both the perception of olfactory pollution by the population and the concentration of gases NH_3, H_2S, CO, O_2 and CH_4 present in the monitoring points were considered.

2 – Material and Methods

The methodology was developed based on existing theoretical framework on evaluation of odor, covering the measurement of gases (H_2S and NH_3), olfactory perception and assessment of climate conditions at the time of measurement. The methodology was validated by evaluating odor at 3 different points (in areas near the tanneries) in the town of Estância Velha - RS - Brazil, on 5 different days in August 2015.

No chemical analysis were applied for detection of odors in this work, and the methodology applied was olfactory evaluation with the aid of a device for measuring gases. 6 evaluators with no previous experience and contact with odors generated by the tanning process were selected for the assessment of olfactory perception. The evaluators filled out a form at each point evaluated. The form aimed to evaluate the perception of each evaluator as to the classes of odorous compounds (Table 1) and the character of the odor Picture 1). Regarding the classes of odorous compounds, the questionnaires considered sulfurous and nitrogenous odor compounds due to the characteristics of tannery emissions.

Quantitative measurements of the gases H_2S and NH_3 were carried out using the equipment Crowcon Gas-Pro portable gas detector (measurement of CO, O2, H_2S and NH_3 - Series 449764/17-001), which has a detection limit of H_2S and NH_3 ranging from 0 to 100 ppm. The temperature and relative humidity were determined through the Thermo Hygrometer MTH-1362W and the wind direction was determined by a Garmin GPS - GPSMAP 62sc.

The quantitative determination of the gases was performed on a 5-minute period, with records being made every minute for each one of the gases, as shown in Figure 2 below:

Location: Evaluator: Date:

Temperature: Relative Humidity: Atmospheric Pressure:

GASES	TIME					AVG.
	1	2	3	4	5	
NH_3						
H_2S						
CH_4						
O_2						

Figure 2 – Gas measurement log

The evaluators received a questionnaire in which, after the stipulated 5 minutes, they were requested to note down their perceptions of the smells in the different places, as shown in Figure 3. This figure shows the questionnaire that classified these perceptions of odors in terms of hedonicity, character and odor characteristic. As for the character and the characteristic, the evaluators were allowed to tick more than one option.

Location: Evaluator: Date:

Hedonicity	**Nature**	**Odor characteristics**
Almost imperceptible, bearable Very weak Medium Strong Very strong, unbearable	Floral Fish Fruity Chemical Medicinal Vegetal Earthy Offensive	Rotten eggs Strong possum Ocher Strong and irritating Strong garlic Pungent and irritating Putrefying fish Pungent and ammoniacal Putrefying meat Rotten fish Fecal, nauseating

Figure 3 – Gas measurement log.

3 – Results and Discussion

Although NH_3 and H_2S gases were not detected during measurements, the evaluators reported the perception of the following odors: rotten eggs, strong smell of possum, rotten fish, putrefying fish, putrefying meat, pungent and irritating, ocher odor, spicy and ammoniacal odor that are related to odorous sulfurous and nitrogenous compounds which indicate the presence of atmospheric pollutants.

As for hedonicity, the prevailing perception was "almost imperceptible", "bearable", followed by the perception "very weak". As for the character, "offensive", "chemical" and "floral" predominated. As for the characteristic of odor, "rotten eggs" was the predominant (sulfurous class), followed by "rotten fish" (nitrogenous class), "putrefying meat" (nitrogenous) and "strong, irritating smell" (sulfurous).

4 – Conclusion

Even if the system has not detected values due to the low concentration of H_2S and NH_3 gases, the evaluators had perceptions of odors characteristic of the same, like rotten eggs (sulfurous) and rotten fish (nitrogenous), gases which are easily noticed by human smell.

Considering there was no detection of measured gases on the assessed spots and that the hedonicity of the odors was considered "almost imperceptible" and "very weak" there was consistency between the gas measurement results and the olfactory perception.

5 – Acknowledgements

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