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Date : January 23rd, 2014

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(by Hans Schieven, CEO of Uniqair Technologies Ltd)

New Odor Sampling Procedure for high humidity air flow from dryers/coolers:

A new odor sampling procedure with nitrogen dilution has been developed by Uniqair and Purdue University's odor lab for odor evaluation of high humidity airflow from petfood dryers, extruder air conveyer (wet cyclones) and coolers.

The sample bags will be pre-filled with a specific quantity of ultrapure nitrogen prior to sampling to:

- prevent or reduce oxidation of the odors in the sample bag and
- reduce interaction with the sample bag surface which is nitrogen pre-conditioned and

- prevent condensation and preserve the sample for more accurate odor concentration test results.

After adding the odor sample from the stack or pilot testunit, the odor lab can determine the added volume and exact nitrogen dilution in the bag. The bag is made of Tetlar or PTFE.

Odor analyzes:

Only an odor lab that can comply to the latest olfactometry standards in combination with a correct odor sampling procedure, is able to measure the odors from petfood processing. The odor test results are used for stack dispersion modelling to calculate the odor concentration at ground level around the plant.

Odor evaluation: odor concentration at ground level before/after treatment:





Analytical testing for the chemicals in airflows from the extruders/dryers/coolers will not provide any clear information about the odor concentration, because:

- It is a <u>cocktail</u> of hundreds different organic components. A single chemical may have a certain odor but it is not possible to calculate the resulting odor if all chemicals are mixed in a cocktail.
- The weight <u>concentration of the odor components is mostly very low</u>, like 10 mg/m3, but the odorconcentration can be very high. Odor concentration = DT (Detection Threshold) or ou/m3 = odor units per cubic meter. 1 DT = 1 ou/m3. The odor concentration is the number of required dilution's with clean air in order for half the population to just being able to detect odor. For petfood dryers and extruders this can range app. from 20,000 to 100,000 ou/m3 (or DT) depending on process conditions, recipe, etc.
- The odor-components with the lowest concentrations (sub-ppb-range) <u>may not be detected analytically</u> by <u>GC or GCMS</u> but the human nose may detect. An example of an odor with a very low threshold is IsoAmylMercaptane = 0.00077 ppb. This is less than 1 part per thousandth of a billionth.
- Each odor-component can mask or amplify another component within the cocktail.

Other factors that make odor emission evaluation complicated:

- Odor is <u>dynamic</u>, since the components and their concentrations will vary in time due to differences in process-conditions, raw material quality and origin, recipe's, etc.
- <u>Particles</u> can generate odor once they are released in atmosphere, especially particles below 1 micron have a large total surface area and can interact with the air. A cold plasma odor oxidizer need to be placed after the cyclone or dust filter to prevent new odors from generating again after treatment.
- Odor can escape out of windows and doors and during outside loading/unloading, which can cause odor and/or dust complaints even if there is no stack emission. A clean environment and "good housekeeping" are important. These so-called 'premise-odors' are at ground level and have very little dilution.
- With a low odor concentration out of the stacks, odor may sometimes still be detected during <u>certain</u> <u>weather conditions</u> when the (humid) plume goes down to ground level quickly, reducing the dilution.
- Odor measurements are expensive and do have a <u>large tolerance</u> on the results. They have to be executed by certified laboratories according the best available standard: CEN13752. This standard is now accepted by ASTM.
- Odor immission in the surrounding area is occurring <u>within 1 to 10 minutes</u> after emission out of the stacks. Odor measurements need to be done as soon as possible after sampling but are officially allowed to be analyzed within 28 hours after sampling. Odors can oxidize or change in the sample bag and odor concentrations are mostly decreasing in time, so this may cause errors.

Odor immission on ground level can be calculated from stack emission measurements and stack dispersion modeling. The actual situation can cause differences with respect to the outcome of the standard calculations due to changing area situation (new buildings, etc.), weather conditions (long hot summer, unusual wind direction etc.) and above mentioned factors. Therefore pilot testing, sampling, odor sample analyzes and stack dispersion modeling need to be done accurately according the highest standards.

Pilot testing: example of a Plasma-Injector pilot test system for cold plasma oxidation







Plasma-Injector stack odor oxidation process (www.uniqair.com):

STACK

The Plasma-Injector is oxidizing petfood odors instantly with oxygen radical injection from ambient air; for example 12,000 cfm (20,000 m3/h) with 9kW energy consumption, reducing odor concentration from app. 20,000 ou/m3 to 2,000 m3/h without using water or any chemicals and no waste. With stack dilution of 2,000 the odor concentration is below 1 ou/m3 (detection threshold) on ground level. Stack dispersion modeling will show the radius from the stack to the 1 ou/m3 detection threshold circle. However some jurisdictions have a limit of 5 ou/m3. This will result in an odor intensity that is "weak". The odor reduction efficiency can be controlled with the energy level duty cycle 0-100% of the plasma reactor. By increasing the frequency from 400Hz to 30,000Hz this is now the only plasma injection system that can generate more activated oxygen for most efficient odor control.

Unlike VOC testing with analytical instruments, the odor lab is utilizing human noses in an odor free lab environment: 6 screened panel members with odor sensing capabilities that reflect the 'average person' according the latest CEN13725 and ASTM odor testing standards. The sensitivity of the assessors noses are measured with a reference gas (n-butanol) and they are only allowed to detect this in a specific range that represents an 'average person'.

To be a panel member, the data collected for that assessor shall comply with the following criteria: - the geometric mean of the individual threshold estimates, expressed in mass concentration units of the reference gas, has to fall between 0,5 times and 2 times the accepted reference value for that reference material (123 μ g/m3 for n-butanol: 62 μ g/m3 to 246 μ g/m3 = 0,020 μ mol/mol to 0,080 μ mol/mol). - the antilog of the standard deviation S(individual threshold estimate) calculated from the logarithms (log10) of the individual threshold estimates, expressed in mass concentration units of the reference gas, has to be less than 2.3.

- for at least one of each twelve regular sample odor detection measurements, the reference gas test has to be measured again in order to record and maintain a measuring history. If the panel member does not comply he/she is excluded from all further measurements until compliance is reached again.

Odor lab:





Odor samples need to be assessed within 28 hours after sampling, otherwise the odor molecules may react with other odor molecules or with oxygen, water vapor, etc. and this will generally reduce the odor concentration. So after pilot testing and sampling, the samples need to be shipped overnight to the odor lab for odor testing the next morning. Since the odors from feed and petfood processing contain a very large (hundreds to thousands) number of organic components in very low weight concentrations (ppm to sub-ppb) in addition to sometimes very large quantities of water vapor, the odors can change rapidly if not diluted and preserved with nitrogen.

Each odor sample is diluted with an "olfactometer". This is a computer controlled mass flow dilution system that is presenting air and diluted odor from a sample bag to the assessors. Air is presented at (2 or) 3 ports; 2 ports present clean odor free air and the third supplies diluted, odorous air. The port with odorous air is presented randomly. The assessors must select which port contains the odor, this is called the "forced-choice" method. First the air from the sample bag will have a very high dilution, like 500,000 dilutions so it cannot be detected. This is including the pre-dilution with nitrogen in the sample bag. Then the dilution is step by step reduced until a value where half of the assessors identify the correct port and this is the threshold concentration; the value of the required number of dilution is the "odor concentration": DT (Detection Threshold) or ou/m3 (Odor Units per cubic meter). This procedure has to be repeated at least 3x in order to increase accuracy.

Some processes or recipes with high fat and protein content can have very high odor concentrations in the (untreated) air from the extruders of more than 100,000 DT or ou/m3. This will require a Plasma-Injector with more energy capacity to oxidize these odors. Most countries/states now recognize the latest European CEN-13725 odor standards and support cold plasma injection odor oxidation for stack odor control as it is a sustainable technology with low energy that does not need any water or chemicals and has no waste.

Chemical substances: some examples with their typical smell (**bold** = detected in recipes with fish)

Hydrogen sulphide	Rotten egg
Methylmercaptan	Cabbages
Ethylmercaptan	Cabbages in decomposition
AllyImercaptan	Garlic
Ammonia	Very prickly, irritating
Methylamine	Fish in decomposition
Indole, scatole	Excrement
Cadaverine	Meat in decomposition
Acetic acid	Vinegar
Butyric acid	Butter rance
Valeric acid	Sweat, perspiration
Formaldehyde	Acre, close
Acetaldehyde	Fruit, apple
Acetone	Sweet fruit
Dimethylsulfur	Vegetables in decomposition
Thiolane	Gas (product for odorization of nat. gas)

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- Uniqair Technologies Ltd (Vancouver, Canada):

The originators of advanced high frequency **cold plasma injection odor control systems** for stack emissions. Unlike incinerators, chemical- or water scrubbers or bio-systems, the PLASMA-INJECTOR[™] is an oxidizer that does not need any chemicals or water and does not generate any waste. Our experience includes over 100 systems for stack odor control: dryers of Petfood, fish feed, etc. Web: www.uniqair.com Email: info@uniqair.com

Visit Uniqair at the upcoming trade shows for the food, feed and petfood industry:
IPPE Atlanta, at booth# 3120, January 28-30, 2014.
<u>http://ippexpo.com/</u>
Petfood Forum Chicago, booth# 308, March 31 – April 3, 2014.
<u>http://www.petfoodindustry.com/PetfoodForum/</u>
VICTAM Bangkok, Thailand, booth# C053, April 8-10, 2014.
<u>http://www.victam.com/?i=189</u>
Petfood Forum Asia, Bangkok Thailand (speaker), April 9, 2014.
<u>http://petfoodforum.petfoodindustry.com/PetfoodForumAsia/Topics_and_speakers.html</u>

- Purdue University (IN - USA)

The Purdue Agricultural Air Quality Laboratory (PAAQL) is part of the <u>Department of Agricultural and</u> <u>Biological Engineering</u> at Purdue University, West Lafayette, Indiana, USA. The PAAQL specializes in odor assessment using field and laboratory olfactometry, chemical analyses using gas chromatography-mass spectrometry with olfactory sensing (GC-MS-O), ion chromatography, closed-cell FTIR spectrometry, and continuous emissions monitoring of ammonia, hydrogen sulfide, carbon dioxide, methane, nitrous oxide, ethanol, methanol and particulate matter. Our research has served industry, government and agribusiness. More info at <u>https://engineering.purdue.edu/~odor/</u>

Schieven is Founder and CEO of Uniqair Technologies since 2004, based in Vancouver-Canada. He invented cold plasma injection technology for odor control and started Aerox (NL) in 1994 as Partner and Director. Cold plasma systems have since been classified as BACT (Best Available Control Technology) by authorities, first in Europe. In 2004, Schieven sold his shares of Aerox to the Verder Group and started Uniqair Technologies Ltd. in Canada to develop a new generation of high frequency plasma injection systems. He has been responsible for over 200 odor control projects and presented information about odor control with cold plasma oxidation to hundreds of companies and to regulators and associations in Europe, Asia and the Americas. (Email info@uniqair.com)

