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Simultaneous chemical and sensory analysis with multidimensional GC-MS-Olfactometry

Simultaneous chemical and sensory analysis with multidimensional gas chromatography-mass spectrometry-olfactometry (mdGC-MS-O) combine classic chromatographic separations with sensory analyses. Trained panelist and human nose is used as a detector simultaneously recording olfactory responses (aromagrams) with chemical separations (chromatograms). Analysis of chromatograms and aromagrams enables separation of odor- (or aroma-) causing compounds in very complex matrixes. Multidimensional chromatography by heart-cutting with Dean's switch enhances chromatographic separations. Combined with the sensory analyses, it allows for isolation and ultimately, identification of odor-causing compounds. Mass spectrometry detection allows for identification and quantification of specific target compounds. The objective of this paper is an introductory overview of simultaneous chemical and sensory analyses using multidimensional GC-MS-Olfactometry.
Key words: Gas chromatography, mass spectrometry, olfactometry, sensory analyses, aroma, odor, multidimensional chromatography, Dean's switch.

Яцек А. Козиел

Көп өлшемді ГХ-МС-ольфактометрия әдісімен бір мезгілдік химиялық және сенсорлық талдау

Көп өлшемді газды хроматография-масс-спектрометрия-ольфактометрия (көГХ-МС-О) әдісімен бір мезгілдік химиялық және сенсорлық талдау классикалық хроматографиялық бөлуді және сенсорлық талдауларды біріктіреді. Үйретілген оператор және адамның мұрны иіс белгілерін (аромаграммалар) және химиялық бөлінуді (хроматограммалар) бірмезгілде жазатын детектор ретінде қолданылады. Хроматограммалар мен аромаграммалардың талдауы өте күрделі матрицаларда иісі бар (аромат) қосылыстарды бөлуге көмектеседі. Дин ауыстырғышы бар көп өлшемді газды хроматография хроматографиялық бөлінуді жақсартады. Сенсорлық талдаулармен үйлесіп, ол иіс шығаратын қосылыстарды изоляциялап, ақырында анықтауға мүмкіндік береді. Масс-спектрометриялық анықтау белгілі нысаналық қосылыстарды идентификациялауға және сандық анықтауға мүмкіндік береді. Берілген жұмыстың мақсаты көп өлшемді ГХ-МС-ольфактометрияны қолданып бір мезгілдік химиялық және сенсорлық талдаулардың кіріспе шолуы болып табылады.
Түйін сөздер: газды хроматография, масс-спектрометрия, ольфактометрия, сенсорлы талдаулар, аромат, иіс, көп өлшемді хроматография, Дин ауыстырғышы.

Яцек А. Козиел

Одновременный химический и сенсорный анализ методом многомерной ГХ-МС-ольфактометрии

Одновременный химический и сенсорный анализ с многомерной газовой хроматографией-масс-спектрометрией-ольфактометрией (ммГХ-МС-О) объединяет классическое хроматографическое разделение с сенсорными анализами. Обученный оператор и человеческий нос используются в качестве детектора одновременно записывающего обонятельные отклики (аромаграммы) и химическое разделение (хроматограммы). Анализ хроматограмм и аромаграмм позволяет разделить соединения, имеющие запах (аромат) в очень сложных матрицах. Многомерная хроматография с переключателем Дина повышает хроматографическое разделение. В сочетании с сенсорными анализами, она позволяет изолировать и, в конечном счете, идентифицировать соединения, вызывающие запах. Масс-спектрометрическое определение позволяет идентифицировать и количественно определять конкретные целевые соединения. Целью данной работы является вводный обзор одновременных химических и сенсорных анализов с использованием многомерной ГХ-МС-ольфактометрии.
Ключевые слова: газовая хроматография, масс-спектрометрия, ольфактометрия, сенсорные анализы, аромат, запах, многомерная хроматография, переключатель Дина.

Introduction

Chemical analyses of odor and aroma is one of the most challenging of analytical tasks. This is because the odor- components are often present at very low concentrations that are below detection limits of chemical detectors. Often, compounds causing odor are present in a complex matrix of less important or irrelevant analytes. Thus, they could be easily overlooked by skilled analysts that naturally focus on chromatographic separations and detector responses. Yet most of 'real-life' matrix are very complex mixtures of hundreds if not thousands of compounds.

It is generally accepted that odors and aromas perceived by human nose are defined a small subset of compounds in these complex mixtures. These 'odor-defining' or 'aroma-defining" compounds are often characterized by low odor detection thresholds (DTs). Odor DTs are defined as gas--phase concentrations of compounds vapors which can be first detected by 50% of human population. Some odor-defining compounds have DTs ranging from part-per-million to below part-per quadrillion. DTs for many compounds are unknown or simply unattainable with current sensitivities of analytical equipment. Thus, human nose used as a detector can be a very useful approach to isolate and identify key compounds in complex mixtures that are responsible for the overall odor and aroma of a complex mixture.

Simultaneous chemical and sensory analysis (e.g., GC combined with sniff port, a.k.a. GC-O) that combines olfactometry and the use of human nose as a detector with conventional gas chromatography can be useful to isolate and separate in many applications. Multidimensional GC-MS-O is few steps ahead of the conventional GC-O approach by offering (1) identification and quantification capabilities with MS and (2) ~ 10-fold increase in chromatographic separation associated with multidimensional GC. Multidimensional GC based on the Dean's switch and heart-cutting (not to be confused with comprehensive GC x GC) allows for additional improvements in isolating odor-defining compounds in very complex mixtures.

The objective of this paper is an introductory overview of simultaneous chemical and sensory analyses using multidimensional GC-MS-Olfactometry.

Methods

Multidimensional GC-MS-Olfactometry systemsare used for the separation, isolation, identification and quantification of compounds in very complex matrixes of hundreds if not thousands of compounds. Olfactometry analyses using human nose as a detector were simultaneous with chemical analysis via the MS. The MDGC-MS-O system is equipped with two columns in series with a system of valves allowing transfer of samples between columns based on the Dean's switch concept (heart-cutting).Schematic is presented in Figure 1.

The mdGC-MS-O (Microanalytics, Round Rock, TX) system consists of a conventional GC-MS (Agilent 6890N GC / 5973 MS from Agilent Inc., Wilmington, DE) and FID with an additional sniff port for olfactory analysis. This system is equipped with 2 capillary columns, i.e., a 12 m x 0.53 mm ID non-polar precolumn (Model SGE BP-5+, SGE, Austin, TX) and a 25 m x 0.53 mm ID polar analytical column (Model SGE BP20, SGE) connected in series along with a system of valves allowing the transfer of a gas sample between the two columns (a.k.a. heart-cutting). The mdGC-MS-O is connected to a computer with a system automation software MultiTrax (Microanalytics) and data acquisition software AromaTrax (Microanalytics), BenchTop/PBM (Palisade Corporation, Ithaca, NY) and MSD ChemStation (Agilent).

The total sample run time for each analysis is typically 40 min. The carrier gas is He (99.995% purity). The oven start temperature is 40 °C and held constant for 3 min. Oven temperature is then increases from 40 °C to 220 °C at a 7 °C/min ramping rate and reaches the final temperature of 220 °C where it is held for 11.29 min. Back flush of the precolumn occurrs from 36 min to 40 min to prepare the system for the next sample. The GC is operated in a constant pressure mode where the mid--point pressure, i.e., pressure between pre-column and column (Figure 1), is always at 5.8 psi and the heartcut sweep is 5.0 psi. The FID connected to the pre-column is maintained at 280 °C with a H_2 flow rate of 35 mL/min, an air flow rate of 350 mL/min, and the makeup N_2 flow rate of 10 mL/min. The FID data acquisition rate is 20 Hz.The MS is connected to the polar column (Figure 1) and the transfer line is maintained at temperature of 240°C.

Simultaneous sensory evaluations are made through the sniff port (Figure 1) equipped with two capillary columns. Only one of them delivers a sample to a panelist depending on the instrument mode (Figures 1), i.e., with or without heart-cutting. The temperature for the sniff port capillaries are set to 220 °C to eliminate vapors condensation. In addition, humidified air is constantly delivered to the sniff port at 8.0 psi to maintain a constant humidity level for the panelists' mucous nasal membranes. The tip of the sniff port is equipped with a glass nose cone (SGE, Part # 093513).

Multidimensional capability is typically used for better separation of gases and odors of compounds associated with swine manure. The MDGC-MS-O system was capable of working in 3 modes, i.e., GC-FID only, GC-FID-O, and GC-MS-O. The MultiTrax system software is used to control the timing of valves and heart-cuts (HC) for each mode. Heartcut is defined as a portion of sample "cut" from the non-polar pre-column and transferred to the polar column. Compounds are further separated on the polar column and then simultaneously analyzed on the mass selective detector and sniff port by a panelists. When the HC valve is opened, the gas sample is transferred from the pre-column into the polar column (Figure 1). When the HC valve is closed, the gas sample stopped flowing into the polar column. Multiple HCs can be selected for one run. The HCs could be as short as 1 sec and long as entire run.

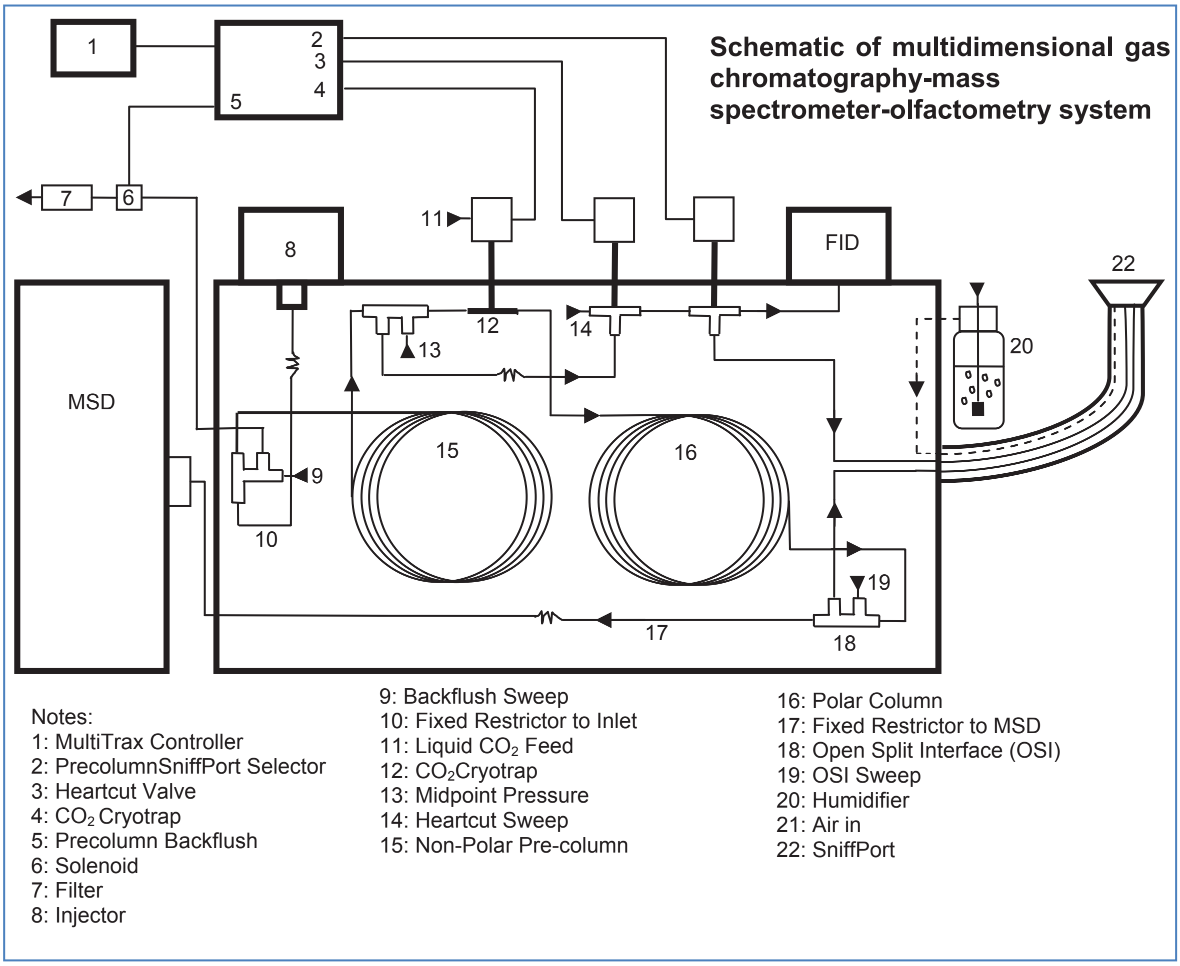

Figure 1 – Schematic of multimensional GC-MS-Olfactometry system for simultaneous chemical and sensory analyses

Figure 2 shows the actual photo of such system at the Atmospheric Air Quality Laboratory at Iowa State University.

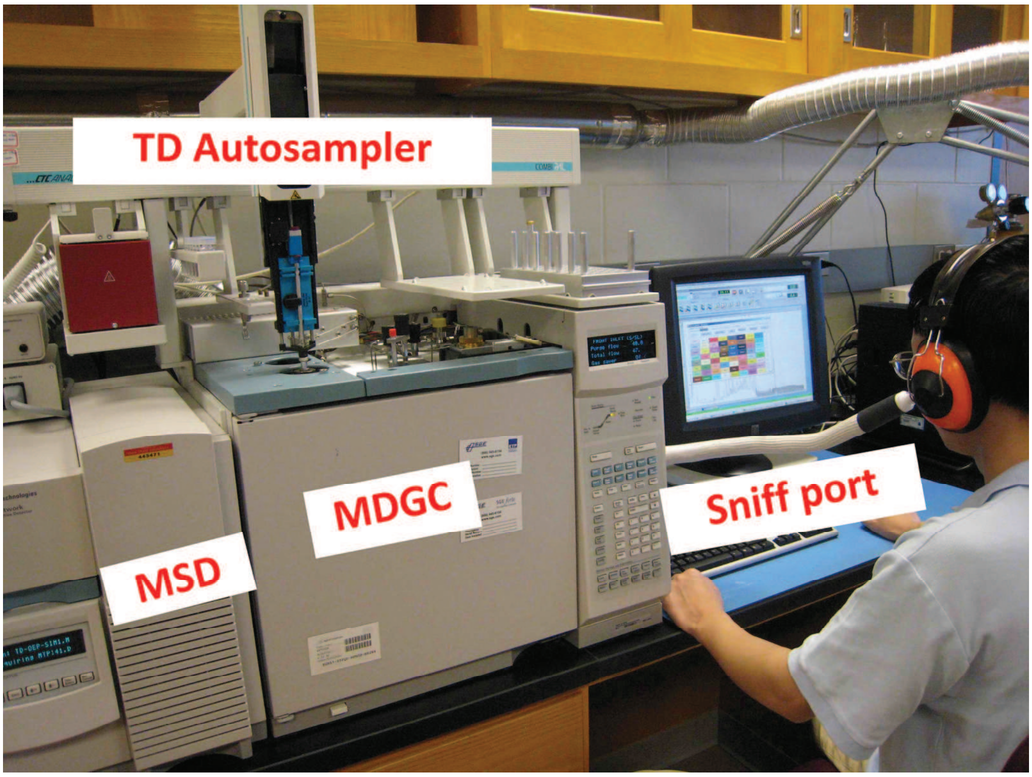

Figure 2 – Multimensional GC-MS-Olfactometry system for simultaneous chemical and sensory analyses. Gas samples could be introduced using either (1) sorbent tubes with trapped gases and the thermal desorption (TD) autosampler, (2) solid-phase microextration (SPME), or (3) direct injection

Results

The following sections further discusses and illustrates how the mdGC-MS-Olfactometry system is used for simultaneous chemical and sensory analyses. Trained panelists places his/her nose at the sniff port (Figures 1 and 2) and records 3 signals simultaneously with on-going chemical analyses. Panelist works with the touch screen panel that is shown in Figures 3 and 4.

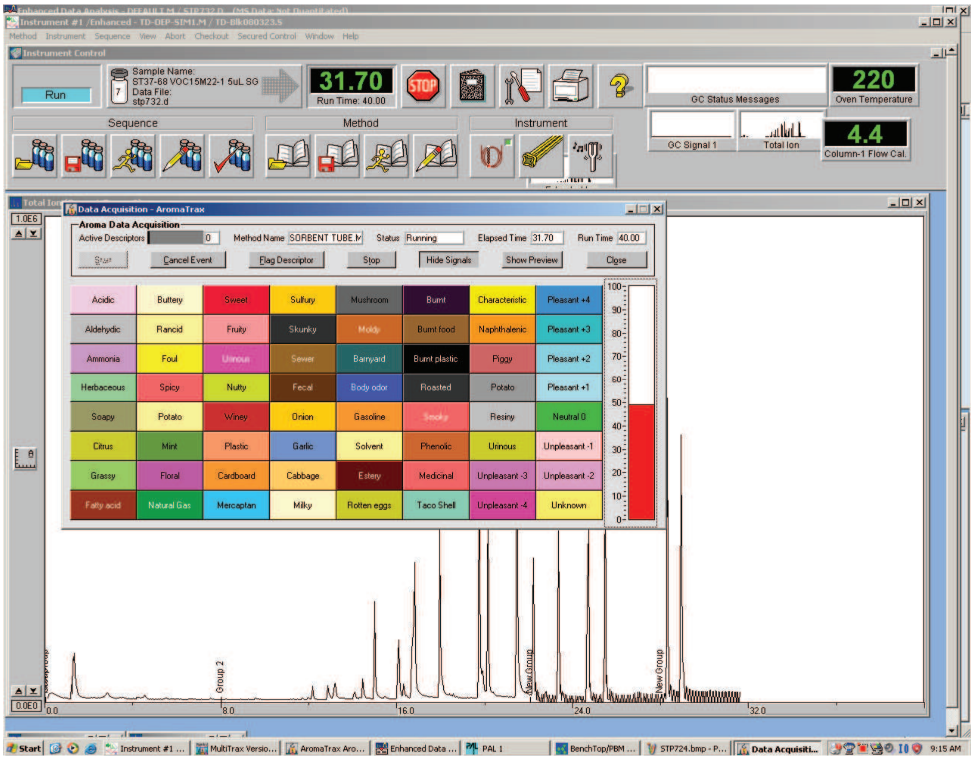

Figure 3 – Full screen view of the sensory panel screen. On-going chemical analyses (chromatogram) can be hidden from the panelist. The colorful, 64 field panel is used to record odor character, odor intensity and odor hedonic tone (close up presented in Figure 4)

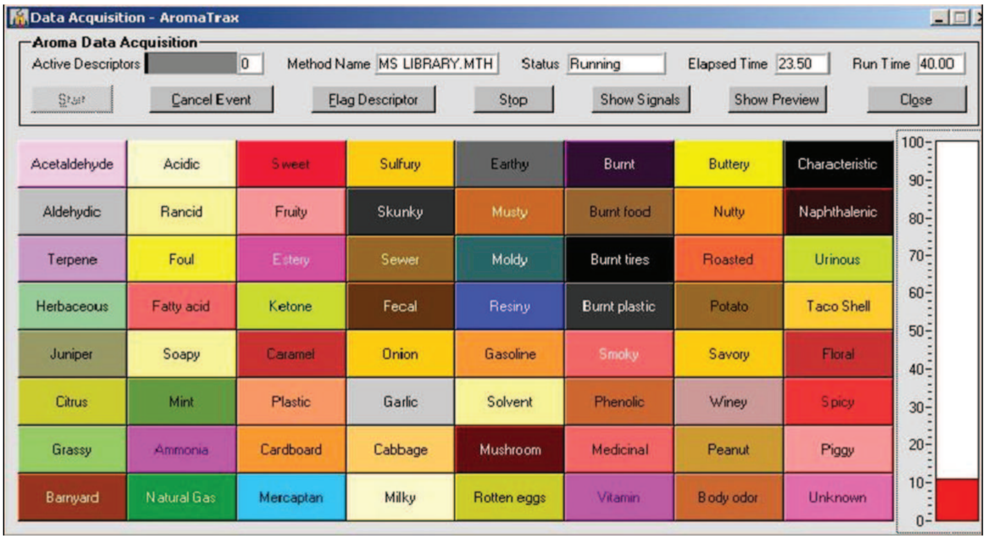

Figure 4 – Odor panel used by trained panelist to record odor character, odor intensity and hedonic tone

Three sets of signals is generated for each sample including the total ion chromatogram (TIC), the FID signal, and the Aromagram. The Aromatrax software is used to record odor 'events'simultaneously with chemical separations and analyses. Panelists evaluate odor character (i.e., what is smells like?) and intensity (how strong is the smell on the scale from 0 to 100%) and the hedonic tone. The hedonic tone is a measure of pleasantness and unpleasantness on the scale from -4 to +4. All odor events re plotted in the aromagram, which included odor event start and end time, odor intensity, odor event area, odor descriptors, and the number of odor events recorded during the entire run. Number of databases exist for designation and use of common odor and aroma characters such as LRI and Flavornet. Sensitivity of human nose and the level of training varies and therefore it is reasonable to expect wide variations especially with not trained panelists. Screening of detection sensitivity, checks with aroma standards, certain panelist etiquette related to diet, personal care, and well-being are crucial for maintaining the quality assurance.

There are three common scenarios:

1. a chromatographic peak and no resulting odor
2. a chromatographic peak and no resulting odor
3. no chromatographic peak and resulting odor

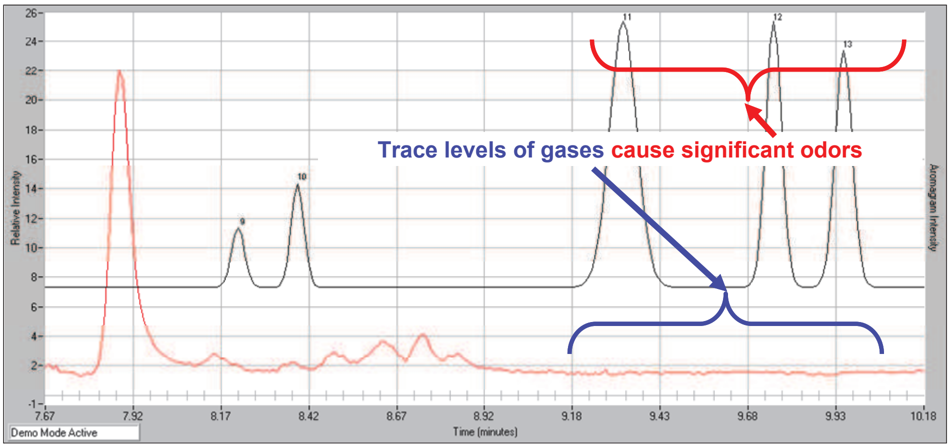

Figure 5 – Comparison of aromagram and chromatogram from simultaneous chemical and sensory analyses illustrating typical scenarios and usefulness of GC-MS-O approach for finding and isolating odor-causing volatiles

The first scenario is quite common, i.e., approximately 2/3[rd] of volatiles in typical environmental samples are present in low concentrations, i.e., below DTs. The second scenario allows for matching of particular odor with causing compound. The third scenario is often most interesting, it is the case when compounds causing odor are likely very potent odorants (low DTs) that are present at very low concentrations. All three scenarios are summarized in Figure 5 below.

Figure 6 illustrates comparison of chromatogram and aromagram of exhaust air from a livestock barn. It is apparent that not only the air sample is complex, but so is the aromagram. As many as 28 separate odor events were reported.

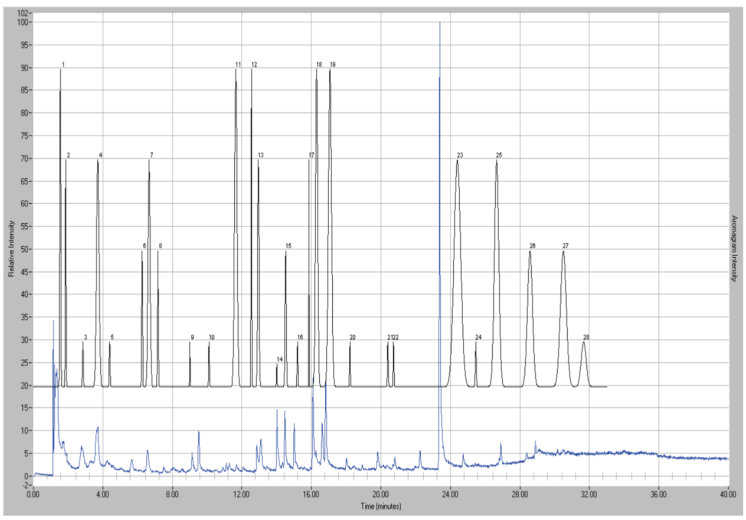

Figure 6 – Comparison of aromagram and chromatogram from simultaneous chemical and sensory analyses of exhaust air from a livestock barn

Table 1 summarizes odor characters, odor intensity and odor hedonic tone for the livestock barn air analyses shown in Figure 6.

Table 1 - Summary of odor characters, odor intensity and odor hedonic tone for the livestock barn air analyses shown in Figure 6.

Event #	Odor Character	Odor Intensity	Start Time	Duration Time	Odor Area	Hedonic Tone
1	Skunky	70	1.48	0.15	1048	-3
2	Skunky	50	1.81	0.11	549	-2
3	Onion	10	2.79	0.14	139	-1
4	Sweet, Buttery	50	3.51	0.41	2046	2
5	Onion	10	4.32	0.15	149	-1
6	Skunky, Sewer	30	6.2	0.14	419	-2
7	Grassy	50	6.5	0.34	1697	2
8	Skunky, Sewer	30	7.11	0.14	419	-2
9	Sewer	10	8.99	0.06	59	-1
10	Onion	10	10.05	0.12	119	-1
11	Mushroom	70	11.45	0.4	2795	2
12	Skunky, Sewer	70	12.5	0.11	768	-3
13	Acidic	50	12.85	0.22	1098	-2
14	Skunky	5	13.97	0.1	49	-1
15	Body odor, Fatty acid	30	14.43	0.2	598	-1
16	Body odor	10	15.14	0.12	119	-1
17	Skunky	50	15.83	0.06	299	-2
18	Body odor, Fatty acid	70	16.13	0.35	2445	-2
19	Body odor, Fatty acid, Sweet	70	16.83	0.49	3424	-3
20	Acidic, Fatty acid	10	18.17	0.12	119	-1
21	Acidic, Fatty acid	10	20.34	0.14	139	-1
22	Burnt, Phenolic	10	20.67	0.13	129	-1
23	Burnt, Phenolic, Medicinal	50	23.87	1.08	5391	-2
24	Burnt, Phenolic	10	25.39	0.16	159	-1
25	Burnt, Smoky, Phenolic, Medicinal	50	26.32	0.7	3494	-2
26	Burnt, Smoky, Roasted	30	28.18	0.8	2396	-2
27	Burnt, Barnyard, Taco Shell	30	30.03	0.95	2845	-2
28	Burnt, Medicinal	10	31.28	0.79	788	-1

Careful analyses of aromagrams with matching chromatograms enables a variety of useful analyses. Some examples of applications are listed below:

1. Identifying links between an odor and a compound causing it
2. Isolating odor-causing compounds in very complex mixtures of volatiles.
3. Determining the effects of concentration on human panelist response.
4. Screening larger population of panelists for responses to certain compound and certain concentration.
5. Breaking down compounds that comprise pleasant or unpleasant smells.
6. Solving odor problems by focusing on mitigation of compounds that really matter,
7. Enhancing aromatic compounds when certain aromas are desired.

Further reading on development and application of mdGC-MS-O technology (specifically at Iowa State Unviersity) could be found in references listed in this article.

Conclusions

Simulaneous chemical and sensory analyses are useful for many real problems common to engineers and scientist working with environment, food, pharmaceuticals, consumer products, personal care products, and quality assurance/quality control. Specifically, this technology can be very useful to isolating, separating quantifying, and ranking odor- or aroma-causing compounds in very complex matrixes.

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