Available online at www.sciencedirect.com
SCIENCE DIRECT®
International Journal of Mass Spectrometry 239 (2004) 203–207
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Quality control of a herb extract using PTR-MS

D. Jaksch[a], E. Hartungen[a], T. Mikoviny[a], G. Abel[b], T.D. Märk[a,c,*]

[a] *Institut für Ionenphysik, Universität Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria*
[b] *Bionorica AG, Kerschensteinerstr. 11-15, D-92318 Neumarkt, Germany*
[c] *Department of Plasmaphysics, Comenius University, 84248 Bratislava, Slovak Republic*

Received 26 October 2003; accepted 22 July 2004
Available online 3 October 2004

Abstract

We have developed an objective method for the determination of a herb extract's quality based on headspace measurements by proton-transfer-reaction mass spectrometry (PTR-MS); this quality was checked by a sensory analysis until now. This novel method enables the company 'Bionorica' to ensure that they are only selling high-quality products and therefore avoid complaints of the customer. The method could be also used for controlling and optimising the production process.

Keywords: Quality control; PTR-MS mass spectrometry; Volatile organic compounds; Headspace; Herb extract

1. Introduction

The company 'Bionorica' produces a valerian extract in large amounts for a single customer Y.[1] Before company Y buys the product it is checked by a sensory analysis. This check is the decisive factor for buying the extract. Since Y is the only customer, it is essential for the producer that the extract passes the sensory check. However, 'Bionorica' has no appropriate method for checking the quality of the extract itself and thus depends on the customer's sensory judgement. In collaboration with 'Bionorica' our aim was to develop an objective method which enables them to control the quality of their extract before selling it to the customer. We measured over the past three years the VOC concentrations in the headspace (HS) of 83 different batches by PTR-MS. Based on the sensory judgement of the customer we were able to find differences in the emissions of 'good' and 'bad' quality samples and developed a method for the quality control of this herb extract. Furthermore, we performed some preliminary measurements in order to evaluate the ability of PTR-MS and the newly developed method for controlling the production process and received promising results. Controlling the production process requires the measurements to be fast. Therefore, we very recently improved the experimental set-up to decrease the measurement time per sample and we will also report on this new development in the present work.

2. Experimental

We measured the headspace of 83 batches (8 with 'bad' quality) of the herb extract by PTR-MS for generating the quality control method. Furthermore, we investigated five different production steps (starting from the original plant material (radix) all the way to the final herb extract) for three batches by PTR-MS to find the first point in time when our method was able to determine the quality. Then we did a field study at 'Bionorica' to check the ability of our technique to control the production process. Very recently, we improved the experimental set-up and adjusted our quality control method.

* Corresponding author. Tel.: +43 512 507 6240; fax: +43 512 507 2932.
E-mail address: Tilmann.Maerk@uibk.ac.at (T.D. Märk).
[1] Name of the company designated Y because of duty to keep confidential.

1387-3806/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2004.07.019

2.1. Proton-transfer-reaction mass spectrometry (PTR-MS)

The measurements were performed using a PTR-MS system that allows an on-line measurement of trace components with concentrations as low as a few parts per trillion in volume (pptv). The method is based on ionizing reactions of H_3O^+ ions with the VOCs to be detected by mostly non-dissociative proton transfer. Most of the common VOCs react with H_3O^+, whereas the other major components present in clean air do not react. The generation of the primary H_3O^+ and the chemical ionization of the VOCs are individually controlled and spatially and temporally separated processes. One important consequence is that approximate absolute headspace concentrations can be calculated without calibration or use of standards. Another big advantage of PTR-MS is that the samples containing the volatile compounds do not need any preparation (pre-concentration or sample dehydration) before being admitted to the PTR-MS. Thus some problems inherent to sampling in alternative methods used so far (e.g., gas chromatography) are avoided and the measured mass spectral profiles closely reflect genuine headspace distributions [1]. The PTR-MS system and measuring procedure has been described in detail in refs. [2,3].

2.2. Sample preparation and analysis of VOCs

2.2.1. First set-up

We filled 2.5 g of the extract in a glassware (radius = 5 cm, height = 1 cm) and equilibrated it in an oven at 30 °C for about 10 min. Then we put the whole sample into a glass vial (diameter = 10 cm, height = 5 cm) with a metal cover with two inlets for measuring the HS concentrations. We detected the VOC concentrations in the HS air of the extract samples on-line with an outdoor air flow of 14 sccm/min through the glass vial to the PTR-MS system. The mass spectrometric data were collected over a mass range of m/z = 20–260 amu. Between measuring different samples we switched on the pump of a bypass line to increase the flow through the Teflon lines in order to quickly reach the initial background concentrations. During the measurements the glass vial was placed in an oven to keep a constant temperature of 30 °C. The lines to the PTR-MS were heated to 40 °C to avoid condensation.

2.2.2. Improved set-up

Since the measurement of one sample took about 30 min (12 min measurement plus about 20 min waiting time for getting back to the initial background concentrations which is necessary to avoid memory effects) with the first set-up we tried a faster way to measure the emissions of the valerian extract that is similar to the 'vial method' introduced by Biasioli et al. [4]. We used a smaller vial (V = 35 ml) covered by a Teflon-coated silicone septum into which we put the 2.5 g sample. This vial with the sample inside was placed in the oven at 25 °C for a fixed time before (1 h) and during (three cycles amounting to a total of 2.4 min) the measurement. The headspace formed in the vial was sampled through the septum by a needle; through a second needle the sampled air was replaced by outdoor air. We took a capillary (heated to 60 °C) instead of the Teflon tube (heated to 40 °C) going directly from the sample vial to the PTR-MS. This novel setup avoids the use of a flow controller where compounds get easily stuck and allowed us to immediately measure the equilibrium concentrations while before we had to average over cycle 10–12 and could not wait for equilibrium in the glass vial (the thermally equilibrated sample was placed in the glass vial just before starting the measurement). The measurement with this improved set-up was four times faster.

3. Results and discussion

3.1. First set-up

A huge number of batches as well as a balanced ratio of accepted and rejected samples is necessary to develop a reliable quality control method. With a total of 83 batches and a ratio of 72:8 (accepted:rejected) we could not quite meet this ideal situation and, therefore could not use standard statistical methods to distinguish the important from the random differences between different samples. We had developed several methods for finding the quality and often had to modify these methods after receiving further batches because previous methods were not sufficiently general. Finally, we arrived at a method to analyze the PTR-MS data and to determine the quality giving satisfactory results for all samples available. This method is based on the measurements of 56 batches. Then we used this method to assign the quality of 25 further batches and compared our results with the ones of the customer's sensory analysis and found perfect agreement.

For generating a method for the quality control of this herb extract we divided 56 batches into four different quality groups depending on the customer's sensory description: 'bad', 'okay', 'good' and 'very good' (group number 0 for 'bad' to 3 for 'very good'). Then we compared the concentrations (transmission corrected and normalized to the total ion counts (TIC)) averaged for each group 0–3 for each detected mass. As an example Fig. 1 shows this procedure for mass 83. We found some differences in the emissions between the 'good' and 'bad' quality samples, determined conditions for the concentration on certain masses and calculated a 'condition value' (CV) that enabled us to assign the consumer's acceptability.

Calculation of the CV: $\mathrm{CV}^p = \sum_{i=1}^{N} K_i \theta(\varepsilon_i [C^p_{m_i} - G_i])$ for sample p, where N is the number of conditions, m_i is the mass, K_i is the contribution of condition i to CV^p, $C^p_{m_i}$ is the VOC concentration of sample p at mass m_i, G_i is the chosen limit, $\varepsilon_i = \pm 1$ depending on the kind of condition (upper or lower limit) we impose, and $\theta(x)$ is the step function ($\theta(x) = 1$ for $x > 0$ and $\theta(x) = 0$ for $x < 0$). Our method contains 20 conditions for concentrations on nine masses that are listed in Table 1.

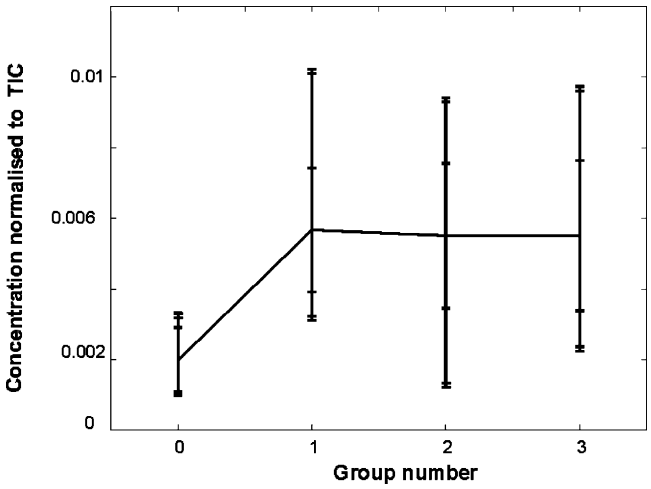

Fig. 1. Concentrations (normalized to the total ion signal (TIC) and transmission corrected) averaged over the groups 0–3, respectively, plus standard deviation, maximum and minimum value against group number. The 'bad' quality samples form the group 0, the 'good' quality samples the groups 1–3 ('okay', 'good' and 'very good').

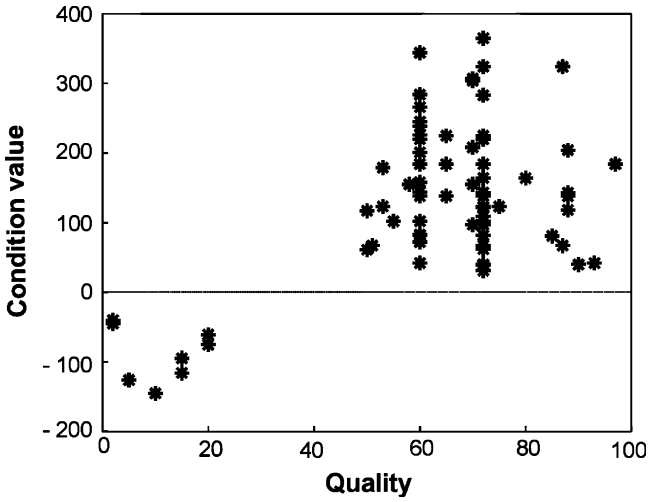

Fig. 2. Condition value (CV) against quality (value related to the customer's sensory analysis, 'good' quality > 50, 'bad' quality < 50). The CV is based on the PTR-MS data. CV < 0 means 'bad' quality and CV > 0 'good' quality. We get a perfect agreement between our results and the customer's sensory test.

If the CV of a batch has a positive sign the quality is 'good', if the CV is negative the quality is 'bad'. We tested this method by assigning the quality of the 25 batches that were not used for the method generation and compared our results with the ones of the customer's sensory analysis and found perfect agreement. Fig. 2 shows the CVs of all investigated samples (the quality value is related to the costumer's sensory description, quality < 50 is 'bad', quality > 50 is 'good'). Thus our method developed allows to determine the consumer's acceptability ('good'/'bad').

Table 1
There are 20 conditions for concentrations on eight masses for calculating the condition value (CV^p) that assigns the quality of a given sample p

i	m_i	K_i	ε_{ia}	ε_{ib}	G_{ia}	G_{ib}
1	29	−40	1	–	4.5×10^{-3}	–
2	29	61	1	−1	2×10^{-3}	4.5×10^{-3}
3	131	99	1	−1	2×10^{-2}	3.5×10^{-2}
4	83	−60	−1	–	2.7×10^{-3}	–
5	83	−30	−1	–	1×10^{-3}	–
6	83	41	1	–	7×10^{-3}	–
7	69	41	1	–	5×10^{-3}	–
8	61	−50	1	–	8×10^{-2}	–
9	61	61	1	−1	4×10^{-2}	7×10^{-2}
10	64	41	1	–	3.5×10^{-5}	–
11	64	41	1	–	3×10^{-5}	–
12	64	−5	1	−1	1.5×10^{-5}	3×10^{-5}
13	125	41	1	–	3×10^{-4}	–
14	125	41	1	–	3.5×10^{-4}	–
15	33	41	1	–	2.01×10^{-3}	–
16	33	−61	−1	–	2×10^{-3}	–
17	33	41	1	−1	9.1×10^{-3}	1.2×10^{-2}
18	43	−1	1	–	8.4×10^{-2}	–
19	43	−20	−1	–	2.5×10^{-2}	–
20	43	41	1	−1	6×10^{-2}	7×10^{-2}

m_i is the mass, K_i is the contribution of condition i to CV^p, $\varepsilon_i = \pm 1$ depending on the kind of condition (upper or lower limit) and G_i is the chosen limit.

3.2. Field study at Bionorica

We measured five production steps (PS 1–5) for three different batches. The production process of the extract is the following: Plant material (PS 1) is put into alcohol (35% vol.) for extraction. The formed liquid (PS 2) consists of 8% dry substance (DS). This liquid is concentrated to 70% DS (PS 3) in a special device under vacuum. Afterwards it is cooked in an open boiler until 80% DS (PS 4) is reached. The extract is ready after diluting it with water to 70% DS (PS 5).

The emissions of the PS could be compared only with the measured VOC concentrations of the final extracts investigated before. Therefore we could determine the quality of the PS if their emitted VOC concentrations fitted into the scheme of the final batches. We measured the PS 1, 4 and 5 under usual conditions described in Section 2.2.1. We had problems to measure PS 2 and 3 because of their high ethanol concentrations. A bypass flow of 250 sccm/min enabled us to detect the emissions of PS 3. The ethanol concentration of PS 2 was too high to do measurements under comparable conditions.

Fig. 3 shows the development of the concentrations on some of the detected masses. These compounds were produced during the production process and some of them had still a quite low concentration in PS 3. We analyzed the data with the method developed and obtained reasonable results for PS 4 and 5. All CVs were positive; therefore the qualities of the batches were good which was in agreement with the sensory analysis of customer Y. We got first hints for the quality starting with PS 4, the last two production steps seem to be the most important ones for the quality.

Furthermore, we successfully used this promising method for investigating the production (cooking) process where we took samples at regular intervals during the process. During this production step the % DS increased from initially about

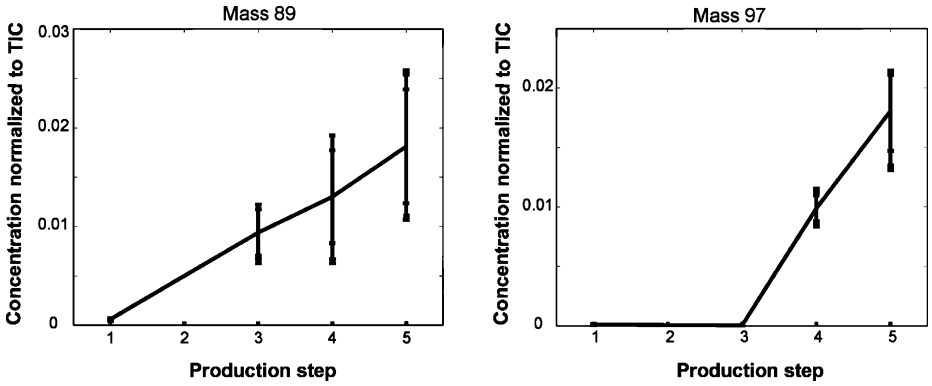

Fig. 3. Normalized and transmission corrected concentrations of mass 89 and 97 averaged over three batches plus standard deviation, minimum and maximum value as a function of the production step (starting from the radix (0) all the way to the final herb extract (5)).

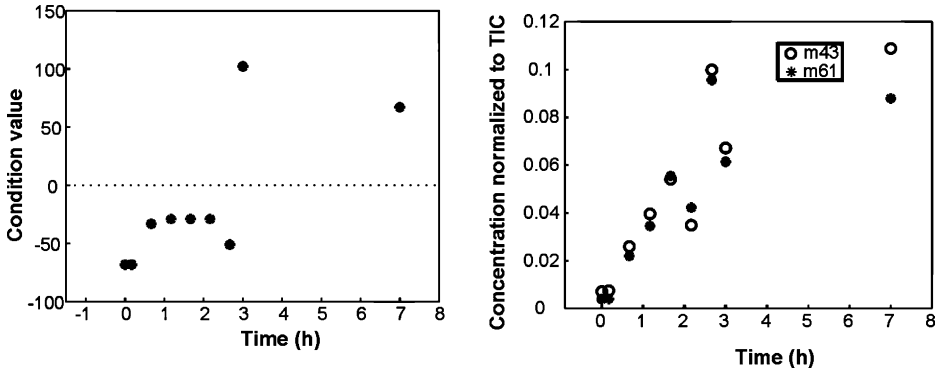

Fig. 4. Temporal development of the CVs and some VOC concentrations of samples taken during cooking in the open boiler.

65% DS to 92% DS because of the water loss while cooking. Then the extract was diluted in water yielding 70% DS. Since the VOC concentrations emitted by the extract decrease with increasing DS we measured not only the samples with their original % DS (Fig. 4) but also the samples after we diluted them to about 70% DS (if the % DS was larger than 70%) giving about the same emission pattern. There are no data between 3 and 7 h because the cooking was stopped for knocking off work. With our method we were able to "watch" how the quality developed: some concentrations increased during the production whereas some decreased; the CV was negative at the beginning, increased and reached a positive value at the end of the production process (see Fig. 4). The goal of this study was to evaluate the ability of this method for controlling the production process.

3.3. Improved set-up

We measured 11 (83 plus another 28 recently produced ones) batches with the improved set-up. Then we adjusted the conditions for our analysis method to the equilibrium concentrations based on the measurements of 36 batches. Table 2 shows the modified conditions and limits. The measured concentrations are normalized to the total ion counts (TIC) and in contrast to former values divided by the corresponding concentrations of a batch that has a very good quality of CV = 93 whose data is given in Table 3. We calculated the condition values with these modified conditions for all 111 samples and plotted them as a function of quality (Fig. 5). Our results are in perfect agreement with the ones of the customer's sensory analysis.

Table 2
Modified conditions

i	m_i	K_i	ε_{ia}	ε_{ib}	G_{ia}	G_{ib}
1	33	−20	1	−1	1.6	1.9
2	33	40	1	−1	0.5	1.2
3	33	60	1	–	2	–
4	47	−40	1	−1	0.17	0.19
5	47	−20	1	–	3.3	–
6	47	40	1	−1	0.3	3.3
7	61	−30	−1	–	0.6	–
8	75	−20	1	–	4	–
9	75	40	1	−1	1.6	4.0
10	81	−40	−1	–	1.0	–
11	81	−50	1	−1	4.5	6.1
12	97	−20	−1	–	0.41	–
13	131	−50	1	−1	0.09	0.11

There are 13 conditions for concentrations on seven masses for calculating the condition value (CV^p) that assigns the quality of a given sample p. m_i is the mass, K_i is the contribution of condition i to CV^p, $\varepsilon_i = \pm 1$ depending on the kind of condition (upper or lower limit) and G_i is the chosen limit.

Table 3
Concentrations (individual ion current divided by the total ion current) of a batch with very good quality

Mass	Concentration
33	0.011271
47	0.058132
61	0.115403
75	0.009250
81	0.000610
97	0.006343
131	0.013722

Measured concentrations are normalized to the TIC and divided by the corresponding concentrations of this batch for calculating the CV.

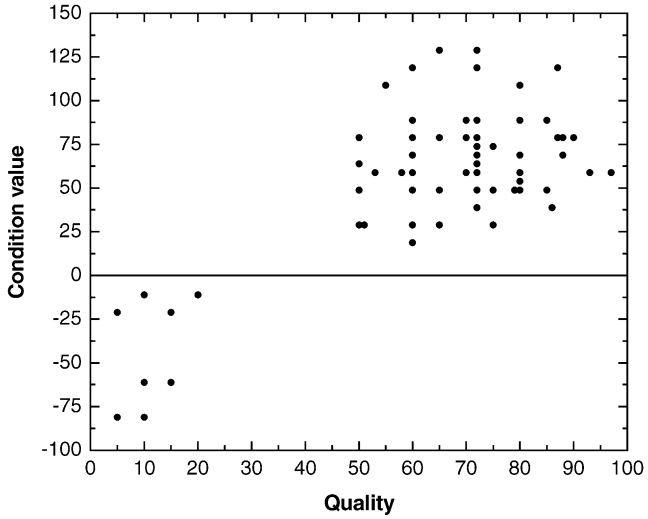

Fig. 5. Modified CV against quality (value related to the customer's sensory analysis, 'good' quality > 50, 'bad' quality < 50). The CV is based on the PTR-MS data. CV < 0 means 'bad' quality and CV > 0 'good' quality. We get a perfect agreement between our results and the customer's sensory test.

4. Conclusion

Our newly developed method allows to determine the quality ('good'/'bad') of the produced extract. We got first hints for the quality starting with PS 4, the last two production steps seem to be the most important ones for the quality. We also used our technique for 'watching' the development of the quality during the last two production steps in a field study at Bionorica and found that PTR-MS in combination with our data analysis method is applicable for controlling the production process.

We measured all 111 batches with the fast set-up. We adjusted the conditions for the 'Hypothesis Generation' to the equilibrium concentrations based on the measurements of 36 old batches and then checked this modified method by assigning the quality of the remaining 47 old and 28 new batches. Comparing our results with the ones of the customer's sensory analysis, we found perfect agreement.

The modified analysis method is based on conditions at seven masses. We immediately measure the equilibrium concentrations with the new set-up. Therefore it would be sufficient to measure one cycle per sample and just those seven masses. Analyzing one sample would therefore take $7 \times 0.2\,\text{s} = 1.4\,\text{s}$ (0.2 s is the measurement time per mass)! This is the basis for on-line monitoring of the emissions during the production process and could be used for controlling and automating the production.

Acknowledgement

This work is partially supported by the Austrian Science Foundation (FWF).

References

[1] C. Yeretzian, A. Jordan, R. Badoud, W. Lindinger, Eur. Food Res. Technol. 214 (2002) 92.
[2] W. Lindinger, A. Hansel, A. Jordan, Int. J. Mass Spectrom. Ion Processes 173 (1998) 191.
[3] A. Hansel, A. Jordan, R. Holzinger, P. Prazeller, W. Vogel, W. Lindinger, Int. J. Mass Spectrom. Ion Processes 149/150 (1995) 609.
[4] F. Biasioli, F. Gasperi, E. Aprea, L. Colato, E. Boscaini, T.D. Märk, Int. J. Mass Spectrom. 223/224 (2003) 343.