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On-line Coupling of Dynamic Headspace Extraction and Ion Mobility Spectrometry for Evaluating Oxidation in Sesame Oil

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Abstract
In this paper, a simple, sensitive and economical method is described for the extraction and determination of sesame oil oxidation by dynamic headspace extraction combined to ion mobility spectrometry (IMS). Hexanal as a reaction product of oxidation, is used to follow the progress of oil oxidation. The optimization of different variables for the extraction step including: extraction temperature, extraction time and flow rate of carrier gas and also for the determination step by IMS including: drift and corona voltages, flow rate of carrier and drift gases, cell and injection temperatures, and pulse width were performed. Under optimum conditions, the calibration curve was linear in the range of 0.10 to 0.50 ng g^{-1} and also the relative standard deviation was 3.0%. The detection and quantification limits were 0.03 and 0.12 ng g^{-1}, respectively. The recovery results for spiked samples (90.0-104.0%) demonstrated the potential of the proposed method for determining of oxidation in sesame oil samples.

Keywords
Sesame Oil; Oil Oxidation; Hexanal; Ion Mobility Spectrometry.

1. INTRODUCTION

Oil oxidation is an undesirable series of chemical reactions involving oxygen that reduces the quality of it. Oxidation process causes rancidity in oil, and also off flavors and smells. Oil oxidation produces a series of breakdown products in several stages, starting with primary oxidation products (peroxides, dienes, free fatty acids), then secondary products (carbonyls, aldehydes, trienes) and finally tertiary products. Type of oil, temperature, light, oxygen, moisture and metals are the effective variables on the oxidation process. Oils containing a large number of polyunsaturated fatty acids are very much at risk to oxidation. This can be related to the presence of reactive double bonds between the carbon atoms of unsaturated fatty acids [1-3]. The primary and secondary breakdown products are considered for evaluating oil oxidation. The most common procedure is the peroxide value (PV) measurement. Other procedures are including: the acid value (free fatty acid), thiobarbituric acid value, iodine value and the volatile organic compounds (smell test). Also, anisidine value (AV) test is an approach to measure secondary oxidation products and Totox value (AV + 2PV) indicates overall oxidation state of oils [4-6]. Several techniques have been used for determining oxidation in oil samples that collected and reported in Ref. [1]. Among, the aldehyde determination; especially hexanal (as a major reaction product of oil oxidation) can be used to follow the progress of oxidation in various food products [7-12].

Ion mobility spectrometry (IMS) which is basically a gas phase ion separation technique, is similar to time of flight mass spectrometry except that it works under atmospheric pressure. It is an analytical technique for characterizing and detecting the chemical substances on the basis of the velocity of gaseous ions in a weak electrical field toward a detector. During drift, ion compounds are separated based on their size, shape, and charge. As a result, various ions reach to the detector at different drift times, which are characteristic of them. The number of ions reaching the detector is a measure of the analyte concentration. IMS has been applied for the determination of an extensive range of compounds due to its excellent sensitivity, quick response and low cost [13-17]. A full description of this technique is provided in books and literature [18-19]. Tzschoppe and coworkers [20] exploited the IMS technique for screening (qualitative detection) the autoxidation of roasted peanuts.

A sample preparation step is often necessary to isolate and concentrate analyte of matrix. In this work, it was decided to develop a simple, sensitive and fast method for the successful measurement (quantification analysis) of oxidation in sesame oil. For this purpose, on-line

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coupling of dynamic headspace extraction and IMS method was proposed. On-line dynamic headspace extraction integrates sampling, extraction, concentration and sample introduction in a simple, solvent-free, and one-step process. The effective variables on extraction and determination were investigated and optimized. Finally, the developed method was applied for the selective detection and determination of hexanal (indicator) in sesame oil as a real sample.

2. EXPERIMENTAL

2.1. Chemicals and sesame oil samples

The chemicals and reagents in analytical grade were purchased from Merck Co. (Darmstadt, Germany). The stock solution of hexanal at a concentration level of 10.0 µg mL^{-1} was prepared by dissolving appropriate amount of it in methanol solvent. Different brands of sesame oil were obtained from local supermarkets (Yazd, Iran) and were kept in refrigerator until analysis.

2.2. Apparatus

In this work, a dynamic headspace extraction design in combination with an ion mobility spectrometer instrument were applied for the extraction and determination of hexanal in sesame oil samples. A schematic view of the configuration and connections in designed system are shown in Fig. 1. The extraction setup was including: sample vial, water bath and carrier gas. Sesame oil (3.0 g) was transferred into sample glass vial (10 mL). It has been placed in a water bath and the sample solution was mixed (Hot plate stirrer, Model: Heidloph). Then, the released hexanal in the headspace of sample oil was delivered to IMS by a carrier gas (N_2) for determination. According to Fig. 1, carrier gas enters and exits from glass vial through teflon tubes which were embedded on the polyethylene cap. In order to avoid the loss of analyte vapor due to its adsorption on the inner walls of teflon tubes and also to obtain the quantitative results, the transfer path length of analyte from vial until the injection port of IMS should be short.

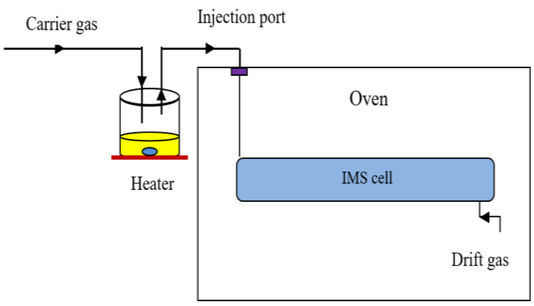

Fig. 1. Schematic diagram of the dynamic headspace extraction and detection system for the determination of hexanal in sesame oil using IMS.

The IMS instrument used in this project was constructed in Isfahan University of Technology, Iran. A continuous corona discharge source in positive mode was utilized as an ionization source. A detailed description of the instrument was reported in Ref. [21]. The total peak area of analyte was integrated over acquisition time and considered as the IMS response. The operational conditions of IMS (drift and corona voltages, carrier and drift gas flow rates, cell and injection port temperatures, and pulse width) were investigated and optimized.

3. RESULTS AND DISCUSSION

3.1. Considerations for choosing a suitable sample preparation

Sample preparation has the potential to influence analytical results. An appropriate sample preparation technique should be used to eliminate the unwanted materials and also to ensure that analyte is present in a suitable concentration level for its satisfactory detection and measurement. According to Fig. 1, a dynamic headspace extraction coupled to IMS has been developed for evaluating oxidation in sesame oil. On-line coupling of dynamic headspace extraction technique has the advantage of being selective for volatile organic compounds over other compounds in the sample matrix. Furthermore, for obtaining the required sensitivity; the length of injection path is short and also the carrier gas is flowed in an appropriate rate. Incomplete and slow transfer of the analyte vapor to IMS causes that it enters as a tailing distribution. As a result, the IMS response and sensitivity decreases. In this work, the analyte transferred directly to IMS, so the extraction, preconcentration, injection and determination were done simultaneously in a single step. The designed system reduced the analysis time and improved the precision and accuracy of the developed method compared to off-line extraction techniques.

3.2. Optimum conditions for extraction

For improving the efficiency, the effect of various variables (extraction temperature, extraction time, and flow rate of carrier gas) on dynamic headspace extraction step was investigated and optimized. Extraction temperature plays an important role on the extracting and releasing hexanal from sesame oil because it influences the mass transfer rate and the partition coefficient of the analyte between the sample phase and the gas phase. In optimum temperature, the analyte quantitative extraction from sample tissue and also the analyte transfer are fulfilled in shortest time. The effect of temperature on the extraction efficiency was studied in range of 20 to 70 ºC. According to Fig. 2, the good results were obtained within 50 to 70 ºC for the extraction of hexanal. At high temperatures, the sample degradation can probably occur. Thus, the 50 ºC was chosen as the optimum temperature. The dynamic headspace extraction presented in this work is an exhaustive extraction. The effect of time; the hold time of sample oil in water bath, on the extraction efficiency was studied in range of 5 to 25 min (Fig. 3). During the extraction time, the valve of carrier gas was firstly closed and after a suitable period (optimum extraction time), it was opened and the extracted hexanal vapor was transferred into injection port of IMS. As shown in Fig. 3, the recovery of analyte increased with increasing extraction time up to 20 min and then it was constant. Consequently, 20 min was selected for future studies. For complete and rapid transfer of the released hexanal from oil sample, the flow rate of carrier gas should be examined and optimized. Selection of the suitable value of this variable can prevent the analyte loss and memory effect because of its adsorption in transfer path to IMS. According to Fig. 1, the carrier gas for extraction step was also used to transfer the analyte vapor from injection port into IMS cell. Based on Fig. 4, 300 mL min^{-1} was obtained as optimum flow rate for carrier gas. The optimum extraction conditions are summarized in Table 1.

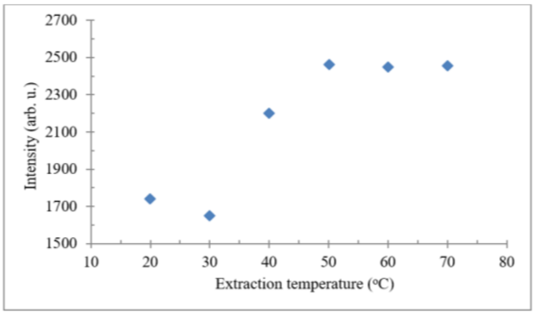

Fig. 2. The effect of the extraction temperature on the IMS response of hexanal. Conditions: extraction time, 25 min; flow rate of gas, 300 mL min^{-1}.

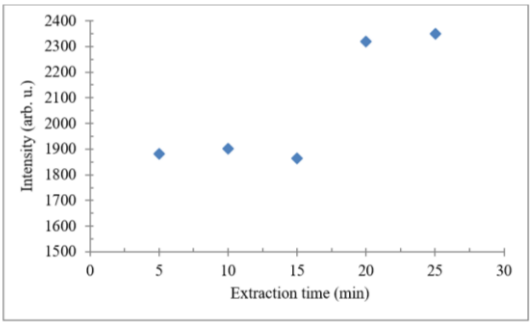

Fig. 3. The effect of the extraction time on the IMS response of hexanal. Conditions: extraction temperature, 50 ºC; flow rate of gas, 300 mL min^{-1}.

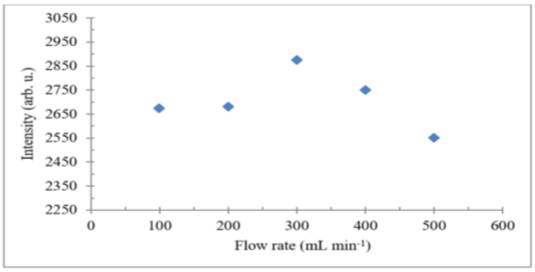

Fig. 4. The effect of the flow rate of carrier gas on the IMS response of hexanal. Conditions: extraction temperature, 50 ºC; extraction time, 20 min.

Table 1. The optimum dynamic head space extraction conditions for the determination of hexanal in sesame oil.

Parameter	Optimum value
Extraction temperature (˚C)	50
Extraction time (min)	20
Carrier gas flow (mL min^{-1})	300

3.3. Optimum conditions for IMS analysis

The effective instrumental variables of IMS including corona and drift voltages, cell and injection temperatures, flow rates of carrier gas and drift gas, and pulse width were investigated. Among, temperature is an important variable. The effect of cell (130-180 ºC) and injection port (190-230 ºC) temperatures on the IMS signal intensity (response) of hexanal were investigated and optimized. According to Figs. 5 and 6, the optimized temperatures were found to be 150 and 200 ºC for cell and injection port, respectively. The operating conditions for obtaining ion mobility spectrum of hexanal in sesame oil sample are presented in Table 2. Ion mobility spectrum of the extracted hexanal in a spiked sample depicts in Fig. 7. According to this Fig., the hexanal spectrum has a peak at about 8 ms which has been well separated from reactant ion peaks (5.5-7.5 ms) and unwanted peaks due to unidentified substances surviving through the extraction step. This demonstrated that the extraction procedure could provide the clean extracts which no extra peaks were observed in region where the analyte appeared.

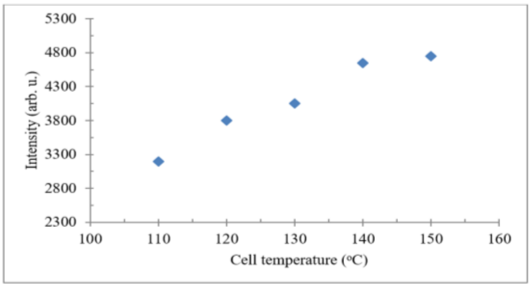

Fig. 5. The effect of cell temperature on the IMS response of hexanal. Conditions: injection temperature, 210 ºC; flow rate of drift gas, 600 mL min^{-1}; flow rate of carrier gas, 300 mL min^{-1}; pulse width, 100 µs; drift voltage, 6800 V; corona voltage, 2300 V.

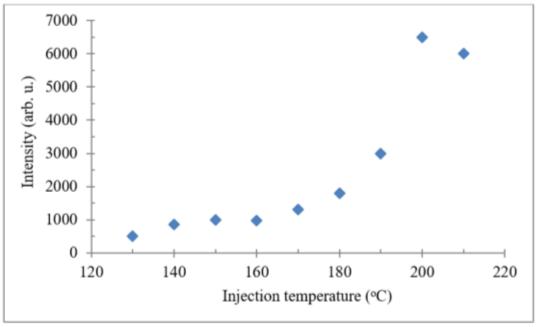

Fig. 6. The effect of injection temperature on the IMS response of hexanal. Conditions: cell temperature, 150 °C; flow rate of drift gas, 600 mL min^{-1}; flow rate of carrier gas, 300 mL min^{-1}; pulse width, 100 µs; drift voltage, 6800 V; corona voltage, 2300 V.

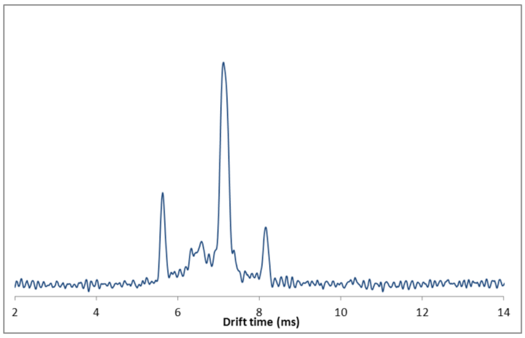

Fig. 7. Ion mobility spectrum of the hexanal extracted by the dynamic head space extraction procedure. Conditions have been reported at Tables 1and 2.

Table 2. The IMS operating conditions for the hexanal determination in sesame oil.

Parameter	Setting
Corona voltage (V)	2300
Drift voltage (V)	6800
Drift gas flow (N_2, mL min^{-1})	600
Carrier gas flow (N_2, mL min^{-1})	300
^{a}Injection temperature (˚C)	200
^{a}IMS cell temperature (˚C)	150
Pulse width (µs)	100

^{a} Injection and cell temperatures were optimized.

3.4.Validation parameters

The analytical parameters of proposed method obtained are shown in Table 3. Under optimum conditions, sesame oil samples (free aldehyde) were spiked with the hexanal standard solution in range of 0.10 to 0.50 ng $_{\text{(hexanal)}}$ g^{-1} $_{\text{(sesame oil)}}$. The injected extracts were sufficiently clean so that almost no matrix effects appeared in the headspace hexanal analysis. Moreover, to avoid matrix effects uses matrix matched calibration standards. The calibration curve was obtained by plotting the IMS response vs hexanal concentration in sesame oil. The linear regression coefficient (r^2) was 0.9907 which indicated good linear correlation. The LOD and LOQ were 0.03 and 0.12 ng g^{-1} for hexanal, respectively. The relative standard deviation (RSD%) for determining hexanal was 3.0%. According to Table 3, the analytical parameters of the proposed method were suitable and also the satisfactory results were obtained for determination of hexanal as a marker to follow the progress of oil oxidation.

Table 3. Analytical parameters for evaluating oxidation in sesame oil by IMS Analysis of hexanal.

Parameter	
Regression equation	Y = 21.94 X + 0.28
LDR (ng g^{-1}, r^2)	0.10 – 0.50 (0.9907)
LOD (ng g^{-1})	0.03
LOQ (ng g^{-1})	0.12
RSD%	3

3.5. Analysis of real sesame oil samples

To evaluate the applicability of proposed method for the hexanal determination in real samples, the spiked and unspiked sesame oils were analyzed. The spiked samples were prepared by adding of analyte to matrix samples in the linear dynamic range of the proposed method. Unspiked sesame oils were also analyzed for determining of hexanal. Based on the recovery results reported in Table 4 (90.0 to 104.0%), the on-line coupling of dynamic headspace extraction to IMS can be a suitable alternative method for determining and evaluating oxidation in sesame oil samples.

Table 4. Results of real sesame oil sample analysis for the determination of hexanal (unspiked and spiked) using dynamic head space-IMS.

Sample	Initial concentration (ng g^{-1})	Added (ng g^{-1})	Obtained (ng g^{-1})	Recovery%
1	0.21	0.22	0.45 ± 0.01	104
^{a}2	0.48	0.41	0.85 ± 0.02	95.5
3	0.39	0.15	0.49 ± 0.01	90

^{a} The sample was diluted with sesame oil free hexanal and then analyzed.

4. CONCLUSION

Oil oxidation is an economic and public health issue and demands different approaches in its restraint. A new configuration of dynamic headspace extraction and IMS (on-line coupling analysis) was developed for the quantification of hexanal as the reaction product of oxidation in sesame oil which providing an alternative method for oxidation diagnosis and analysis. This design presented good results in terms of analysis time, simplicity and sensitivity in evaluating oxidation in sesame oil and therefore, can be applied in routine laboratories without need to solvent and the separation technique. Furthermore, there is a great potential of using the proposed method for other oil samples and make it attractive among green extraction techniques.

Acknowledgement

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استخراج فضای فوقانی دینامیکی جفت‌شده بصورت برخط با طیف‌سنجی تحرک یونی برای ارزیابی و سنجش اکسیداسیون در روغن کنجد

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چکیده

در این مقاله، یک روش ساده، حساس و مقرون به صرفه برای آشکارسازی و تعیین میزان اکسیداسیون در روغن کنجد با استفاده از تکنیک استخراج دینامیکی از فضای فوقانی در ترکیب با روش طیف‌سنجی تحرک یونی توصیف شده است. از هگزانال بعنوان یک محصول فرآیند اکسیداسیون، برای دنبال کردن پیشرفت واکنش اکسیداسیون روغن استفاده شد. بهینه‌سازی متغیرهای مرحله استخراج شامل: دمای استخراج، زمان استخراج، و سرعت جریان گاز حامل و همچنین متغیرهای مرحله اندازه‌گیری با طیف‌سنج تحرک یونی شامل: ولتاژهای شناوری و کرونا، سرعت جریان گازهای حامل و شناوری، دماهای سل و محفظه تزریق و پهنای پالس انجام شدند. در شرایط بهینه، منحنی درجه‌بندی در محدوده ۰/۱۰ تا ۰/۵۰ نانوگرم بر گرم خطی بود و همچنین انحراف استاندارد نسبی ۳/۰ درصد حاصل شد. حدود تشخیص و تعیین به ترتیب، ۰/۰۳ و ۰/۱۲ نانوگرم برگرم حاصل شد. نتایج بازیابی برای نمونه¬های تزریق شده (۹۰/۰–۱۰۴/۰٪)، توانایی روش پیشنهادی برای تعیین میزان اکسیداسیون در روغن‌های کنجد را نشان می‌دهد.

واژه‌های کلیدی

روغن کنجد؛ اکسیداسیون روغن؛ هگزانال؛ طیف سنجی تحرک یونی.