

Development a Sensitive Method Using Gas Chromatography-Ion Mobility Spectrometry for Rapid Detection of N,N-Dimethylacetamide in Air and Exhaust Gas

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Abstract: A comprehensive analytical method was developed for determination of N,N-dimethylacetamide (DMAC) in air and exhaust gas by gas chromatography-ion mobility spectrometry. When the concentration of DMAC was 0-5ppm, the standard curve was established by Boltzmann equation method. The detection limit was 0.003ppm and the average recoveries were 93.0% ~ 107%, the method has high sensitivity, good precision and good qualitative ability, and can be better adapted to DMAC laboratory and on-line detection in ambient air and exhaust gas.

Keywords: Odor; Gas Chromatography Ion Mobility Spectrometry; N,N-Dimethylacetamide

1. Introduction

Odoriferous pollutants refer to any gaseous substances that stimulate the sense of smell and cause unhappiness to people and damage to the living environment. Malodorous gas makes person breathe not smooth, disgusting vomit, irritability, giddy brain bilges, send a person to fume down even, density is high, still can make a person suffocate and die. Odorous substances in odorous gases mostly have the characteristics of odor, volatility, low olfactory threshold, difficult to control and unstable odor property [1], and may contain many toxic and harmful substances, which may have serious implications for Human Health and Environmental Sustainability [2]. Is a typical waste gas pollution, but also the focus of current complaints. Up to now, there are thousands of kinds of malodorous gases that can be detected by human's sense of smell. At present, the odors were detected by gas chromatography [3], gas chromatography-mass spectrometry (GC-MS) [4], electronic nose sensor [5] and so on. N, N-Dimethyl Acetamide (DMAC), as the

important chemical material and excellent solvents, are widely applied to the productive process of polyurethane, acrylic fibers, aramid fiber, dye, coating and so on. DMAC have stable chemical properties. They will give rise to a large number of residual in the process of the textile production and processing. And it will seriously harm human health if people contact the textile with DMAC for a long time, because they have a variety of biological toxicity. In order to reduce the DMAC's harm for people [6-10]. The international Oeko-Tex Association have adjusted the Oeko-Tex Standard 100. Their content is limited in the air. The detection analysis, for air's DMAC has become a heated topic in recent analytical chemical research.

DMAC analysis can be conducted using validated analytical methods with good sensitivity and precision such as HPLC method [11]. The drawbacks of the methods mentioned above were that most of them have long run times, tedious sample preparation and complex instrument. Therefore, there was a need for rapid, cheap and reliable methods that can be conducted and interpreted by users who was closed to the site of contamination.

Gas Chromatography Ion Mobility spectrometry is a new technique developed in recent years. Its working principle is shown in figure 1, Gaseous molecules ionize molecular ions under the action of radiation released from tritium source. Molecular Ions are introduced into a linear electric field, a constant velocity, known as the migration rate, is obtained through a series of interactions such as collision with the reverse drift gas molecule and the electric field force. The ion migration velocity is proportional to the electric field intensity e : $VD = Ke$. In the Formula K is a constant which is related to the relative molecular mass of the Molecular Ion and its collision cross-section with the drift gas molecule under the condition that all the parameters of the equipment are fixed, therefore,

the molecular ions with different relative molecular mass and structure can be separated in the electric field, and finally each of them forms a current pulse on the detector. According to the relative migration time of the compounds and the fitting degree of the gas retention index with the reference material, the compounds were qualitative and quantitative according to the signal intensity. Ion Mobility Spectrometry (IMS) has a high sensitivity to compounds containing S, O, N, Halogen and so on, and is now used for flavor detection [12-15].

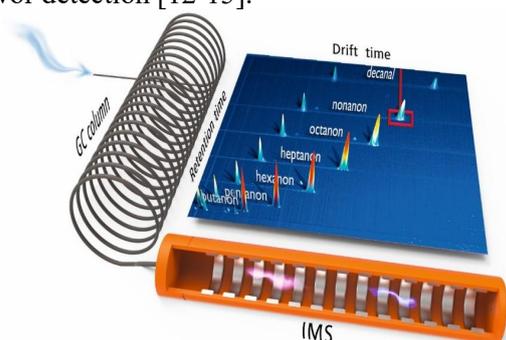


Figure 1. Schematic Diagram of GC-IMS

In this study, we develop a rapid on-site detection of DMAC in the ambient air and exhaust gas. This method was intended as a screening facility, complementary to the conventional quantitative method, but not replacing it. This approach results saved both time and costs, making it useful for companies without access to sophisticated equipment to meet the requirements of the rapidly detection. The establishment of this method can effectively solve the problem of slow detection time of odorous substance.

2. Materials and Methods

2.1 Chemicals and Materials

DMAC standard liquid (DMAC, 99.9%) was purchased from (China). DMAC standard gas ((200ppm) was purchased from (China) liquid standard, high purity nitrogen (99.999%), TEDLAR air bag, Teflon air bag, polyester air bag, gas meter, C4-C9 N-ketones (n-butanone - n-nonone) mixture (corrected retention index) Instruments: Gas Chromatography Ion Migration Spectrometer (GC-IMS), Gas Chromatography (GC).

2.2 The Instrument Condition

Reference conditions for gas chromatography:
GC: Column type: WAX, 15m long, inner diameter 0.53mm, film thickness 1 μ m; Column

temperature: 70°C (constant temperature mode);
Carrier gas: N₂, 0-2min: 5ml/min, 2-10min, linearly rising to 100ml/min;
IMS: Ionization source: tritium source;
Temperature: 45°C; Drift gas: N₂, 150 mL/min;
Positive ion mode Six way valve: 70°C;
Quantitative loop: 1ml

2.3 The Drawing Standard Curve

DMAC uses the dynamic gas distributor to configure the concentration of: 0, 0.5ppm, 1ppm, 2ppm, 3ppm, 4ppm, 5ppm standard gas for measurement, pipeline temperature control: 70°C constant. The results were fitted by Boltzmann equation. Set up the standard curve.

2.4 The Sample Collection

The waste gas outlet of the production workshop and the factory boundary of the enterprise were selected for organized waste gas monitoring.

3. Result and Discussion

3.1 Determination of Monitoring Factors

Using a dynamic gas mixing instrument, the standard gas of DMAC and high-purity nitrogen gas are mixed in a certain proportion to prepare gases of different concentrations, which are directly introduced into the gas chromatography-ion mobility spectrometry combined instrument. The gas chromatography-ion mobility spectrum of DMAC single molecule gas is shown in Figure 2. DMAC shows two signals. By analyzing the molecular structure of DMAC, since the chemical bonds of the nitrogen atoms in DMAC are not saturated and there are vacant lone pairs of electrons, while the adjacent hydrogen atoms have vacant hybrid orbitals, when the two molecules approach each other, a conjugation is formed, resulting in the formation of a dimer.

Through test data, it is found that there is a dynamic equilibrium between the monomer and the dimer. As the concentration increases, the concentration of DMAC monomer tends to saturation after reaching a certain value, while the signal of the dimer form still has a stable growth. By superimposing the spectra of different concentrations of DMAC, as shown in Figure 3, the monomer of DMAC has already reached saturation at a lower concentration (2ppm), while the data of DMAC dimer still shows a good signal growth. DMAC dimer still shows good signal growth at 5 ppm, which

conforms to the Boltzmann equation. There is a wider detection range. Therefore, in this study, the signal of DMAC dimer is used for the fitting of the standard curve.

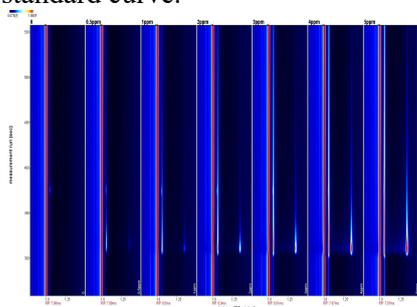


Figure 2. IMS of DMAC at Different Concentrations

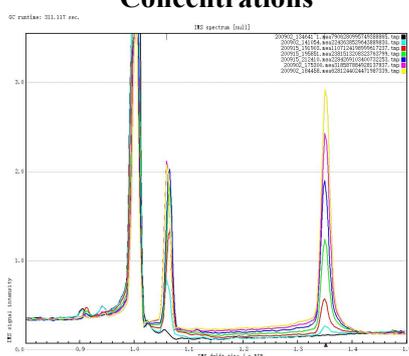


Figure 3. Peak Value Superposition Diagram of Ion Mobility Spectrum of DMAC

3.2 Test Sensitivity, Specificity and Stability

The established standard curve is shown in Fig. 4. When the SN=3 of the instrument, the detection limit is 3 times of the baseline noise of 6mV. The results showed that the detection limit of DMAC in the atmosphere by GC-IMS was 0.003ppm (0.01mg/m³). Compared with the existing national standards for workplace detection, the detection limit of DMAC is 1.69ppm (6.6mg/m³) after 15L sampling enrichment.

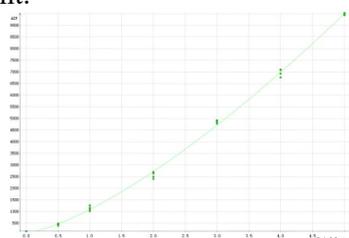


Figure 4. DMAC Standard Curve of Gas Chromatography Ion Mobility Spectrometry

Boltzmann Equation: $AIP = P_1 + (P_0 - P_1) / (1 + \exp((\log(x) - P_2) / P_3))$
 $P_0 = 1.45229 * 10^7, P_1 = 92.1162, P_2 = 6.88884, P_3 = -0.71914$

Note: AIP refers to the peak strength value, using the peak volume, log refers to base e, which we usually write as ln.

The reliability of the GC-IMS assay was determined by carrying out the test with the uncontaminated samples spiked with DMAC and analyzed. Dilute the solution with methanol to the corresponding concentration by DMAC, then take 1μL standard solution and pour it into polyester air bag, fill it with 5L nitrogen for dilution, and put it into the oven (60°C) to bake for 10min. Samples of 0.1ppm and 3ppm were configured for determination, and the results of four times were shown in Table 1.

Table 1. Results of Recovery by Labeling

Spike level	GC-IMS (ppm)				Average	RSD
0.1ppm	0.094	0.081	0.093	0.104	0.093	10.13%
3ppm	3.327	3.341	3.186	2.992	3.211	5.05%

3.3 Select the Sample Container

Through distribution device directly to the nitrogen gas into air pocket, put air pocket in 20°C, 30°C, 40°C, 50°C, 60°C of series thermostat 30 min, then were determined by testing found that Tedlar bag, Teflon bag, polyester bag, only a blank can satisfy the test requirement of polyester bag, Tedlar bag, Teflon air pocket of background value is very high, not suitable for sample collection.

Through the air distribution meter will be configured DMAC into the polyester air bag, and then put the air bag into the 20°C, 30°C, 40°C, 50°C, 60°C series thermostat for 30min, and then test, to judge the polyester air bag on DMAC adsorption. The test found that with the increase of temperature, polyester air bag absorption of DMAC becomes smaller, but still can not hide the experimental requirements, through the air distributor will be configured DMAC into the air bag, and then injected 1 microliter of methanol, then put the air bag into 20°C, 30°C, 40°C, 50°C, 60°C series of thermostat for 30min, and then determined. Methanol was added to increase the concentration of DMAC in the aerosol. The results showed that under the condition of 60°C, the measured concentration of DMAC and the real concentration were basically the same, which solved the interference of sampling materials on DMAC test.

DMAC gas was prepared by gas distributor and standard gas for testing. It was found that the peak strength of DMAC increased gradually in the test results of the same concentration, which

may be related to the residual DMAC and pipeline adsorption. Stable standard curve was also obtained through passivation pipeline and heat preservation of distribution inlet sample pipeline. However, due to the poor stability of the standard gas, it is suggested to use the standard liquid configuration method to establish the standard curve.

3.4 Analysis of Gas Samples

The pollutant concentrations at 6 sampling points were quantitatively measured this time. The specific detection results of each sampling point are shown in Table 2. The 5 factory boundary points detected in this test are all sensitive points in the surrounding environment of the factory, and their pollutant concentrations directly reflect the degree of the factory's impact on the external environment. From the detection data, the pollutant concentrations at the factory boundary points are overall stable and evenly distributed, with a concentration range of 0.914 to 1.001ppm, and the fluctuation range is small, with the maximum difference being only 0.087ppm.

After calculation, the average concentration of the 5 factory boundary points is 0.96ppm. Among them, the concentration at the north side of the factory boundary is the lowest (0.914ppm), and the concentration at the west side of the factory boundary is the highest (1.001ppm), with a small difference in concentration between the two, indicating that the pollutants diffuse uniformly around the factory boundary and no abnormal high local concentration phenomenon occurs. Combined with relevant detection standards and the concentration levels of similar enterprises' factory boundaries, the concentrations of each factory boundary point detected in this test are all at a relatively low level, without any risk of exceeding the standard, indicating that the factory's pollutant emission control effect is good.

The process gas treatment device is the core point of pollutant generation and treatment in the factory. Its detected concentration (12.337 ppm) is significantly higher than that of the factory boundary points, and it is the point with the highest pollutant concentration in this test. Its concentration is approximately 12.8 times that of the average concentration of the factory boundary, and it can be determined that this device is the main concentrated source of pollutants in this detection area. Its operating

status directly affects the pollutant concentration level of the surrounding environment.

Gas chromatography with reference to the workplace monitoring method (China), we analyze the outfalls sampling and, the results of the analysis of 2.59ppm (10.5 mg/m³), the results of the two kinds of instrument of testing deviation, is mainly due to the sampling time in the workplace than household, is a period of time the average concentration of reaction, GC-IMS sampling is rapid, direct determination of reaction is the instantaneous concentration of sample.

Table 2. Actual Sample Determination Results

Sampling points	GC-IMS (ppm)
East of factory boundary	0.928
South of factory boundary	0.975
West of factory boundary 1	0.998
West of factory boundary2	1.001
North of factory boundary	0.914
The eliminator of process gas	12.337

4. Conclusions

This study has successfully established a rapid and direct monitoring method for the determination of DMAC in ambient air and exhaust gas. The method has high spirit density, good accuracy, the machine is small in volume, less gas consumption, and can be used for on-line monitoring of ambient air under appropriate circumstances.

The developed here shows the GC-IMS technology can be applied to the detection of DMAC in gas at concentrations at or above 0.003ppm. Compared with other methods, the GC-IMS has many advantages. First of all, it was a simple method. The test results can easily finished. Secondly, the risk to the environment is decreased during the sample collection operation.

In conclusion, the developed in this study can be used as convenient tools for the rapid and pretreatment-free screening of DMAC residues in gas samples.

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