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Technical Cleanliness analysis by Pyr-GC/MS method-performance study

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Short Report

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Abstract

Technical Cleanliness (TC) as a parameter of industrial products requires companies to define and control cleanliness of their finished goods and production premises. Besides well-established methods recommended in VDA 19 and ISO 16232 standards, the Pyr-GC/MS method can also be effectively applied for cleanliness analysis.

In this paper we have investigated performance of Pyr-GC/MS method in terms of the size of particulate contaminant(s) possible to be reliably identified by this method. This parameter, better known as Limit of Detection (LOD), is crucial for expressing limitations of Pyr-GC/MS technique and for comparing it to other methods currently applied to TC analysis. The PVC polymer was chosen for its good solubility in THF creating solutions which provided control over amount of sample introduced for Pyr-GC/MS measurement(s). From the studied solutions, the 0.5 ng LOD was reached as a result reliable for TC analysis, which corresponds to 8.8 µm (spherical)particle size.

1. Introduction

Technical Cleanliness is an important study of contamination character, whether particulate or molecular. As the trend of downsizing of products continues across all fields of industry, characterisation of contaminates poses a growing need for companies all around the world. Our paper addresses this challenge and provides performance-expression of another tool for identification of particulates.

In our previous paper [1], we have shown that the Pyrolysis GC/MS method is suitable for characterisation of particulate contaminants, especially if organic-based. Among studied samples [1] all were determined uniquely in terms of qualitative characterisation of their chemical make-up and, additionally, their originating source when considering common materials used at the production site

Although Pyr-GC/MS has proven its applicability for determination of organic-based particulates, its performance has not been studied yet. When it comes to definition of performance of any method utilised in technical cleanliness agenda, the size of the smallest particle reliably determined is mostly used as a comparative parameter among recommended methods. For example, several leading companies in technical cleanliness analysis advertise their products as capable of detecting particles as small as follows:

- 5 ums for Leica or Keyence companies, both manufacturing optical microscopes equipped with LIBS spectroscopy feature [2,3]
- 5 ums for Zeiss company, manufacturing scanning electron microscopes with EDS feature [4]

Although micrometre [um] is a generally used and accepted unit in the field of microscopy, it is not as usual unit for expressing result of Pyr-GC/MS analysis. Therefore, we have decided to investigate performance of Pyr-GC/MS method in terms of the standard parameter, i.e. defining the Limit of

Detection in the unit of [ng], but also recalculating this result into unit of [um] for a theoretical particle of a spherical shape.

2. Materials and Methods

2.1 Samples

In our previous paper we have studied common contaminants from an assembly line [1]. This setting was good to show applicability of Pyr-GC/MS method for a real-life scenario, but these samples are not the best choice for an LOD study, mostly because of their industrial-grade purity state. Therefore, we have decided to use PVC polymer (Fujifilm Wako Pure Chemical Cor., specific gravity 1.385) with p.a. purity grade. We have dissolved the PVC in THF (tetrahydro- furan) of p.a. purity grade (Fujifilm Wako Pure Chemical Cor.). In this manner the amount of PVC is easily controllable allowing for proper identification of the investigated LOD parameter.

2.2 Apparatus and measurement conditions

Analysis of the samples was carried out with multi-shot pyrolyzer (Frontier Laboratories Ltd., EGA/PY-3030D), which was connected to the injector of a gas chromatograph coupled to a mass spectrometer (Shimadzu Corp., GC-MS-QP2010 Ultra). For chromatographic separation, the SH-1MS capillary column (15 m × 0.25 mm × 0.10 μm) coupled with 2m guard column was used. The carrier gas was helium (99.995%) with a constant flow of 1.0 mL min^{-1} and sampling time of 1.25 min. The injector and transfer line temperatures were set to 300 °C. The oven temperature program started at 50 °C, keeping this temperature for 2 min and then increasing it to 300 °C by 20 °C.min^{-1}, which was held for 14.50 min. The overall duration of one analysis was 30min, a commercial-friendly option. Operation conditions for electron impact (EI) mass spectrometer were as follows: ionizing voltage of 70 eV and SCAN range from *m/z* 29 to *m/z* 750. Identification of the detected compounds was performed by comparison with the NIST 2023 library.

2.3 Pyrolysis temperature

Pyrolysis temperature was set to 600°C as in our previous paper [1], providing sufficient thermal degradation conditions for PVC material.

3. Results

3.1 Qualifier of PVC

Thermal degradation of Poly-vinyl chloride has been studied substantially over time. Decomposition takes place in two stages with the latter stage yielding aromatic substances as final products. Out of these aromatic compounds, we have chosen Naphthalene as the qualifier of PVC, with molecular ion (*m/z*) having value 128 [5].

3.2 Limit of detection

1.0 mg of PVC was weighed and dissolved in 1 ml of THF. Out of this solution (1000 ppm) consequent solutions of 100ppm and 10 ppm were prepared. Amounts of 10 ng, 1.0 ng and 0.5 ng were introduced for Pyr-GC/MS measurements(5-times) out of these solutions. The schematic pyrograms are displayed in Figure 1.

The well-known signal-to-noise (S/N) ratio was chosen as a parameter to define the LOD of the described method. As it is very important to decide the character of unknown particulate contaminant with a level of certainty, we have decided to define LOD for a more reserved value of S/N≈ 10, though lower values can be generally accepted in gas chromatography. This approach does provide for a reasonable, realistic and field-applicable evaluation of Pyr-GC/MS's performance capabilities in TC analysis. Results of S/N ratio of pyrograms mentioned above are displayed in Figure 2. The average S/N value for 10 ng, 1.0 ng, and 0.5 ng measurements was 39.36, 19.42, and 11.14, respectively. As some of the S/N values for 0.5 ng measurements were nearing or below value of 10, we consider this result as limit value thus expressing reliable LOD as 0.5 ng PVC. After recalculating this result for a spherical-shape particle using specific gravity from specification of PVC, the result can be expressed as a particle of 8.8 μm diameter in size.

4. Conclusion

Technical cleanliness analysis is an emerging field of industrial chemical analysis with significant potential. Various methods are recommended as suitable for this type of analysis with Pyr-GC/MS being also applicable.

While Pyr-GC/MS can be effectively applied to characterise organic-based particulate contaminates, it is also important to express its performance capabilities. The Limit of Detection parameter can be used for this purpose. In this paper we have shown the LOD to be 0.5 ng of PVC. This standardised result can be re-calculated to a spherical-shape particle size of 8.8 μm.

Declarations

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Supplementary data

Electronic Supplementary Material associated with this article can be found in the online version of this paper (DOI:)

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Figures

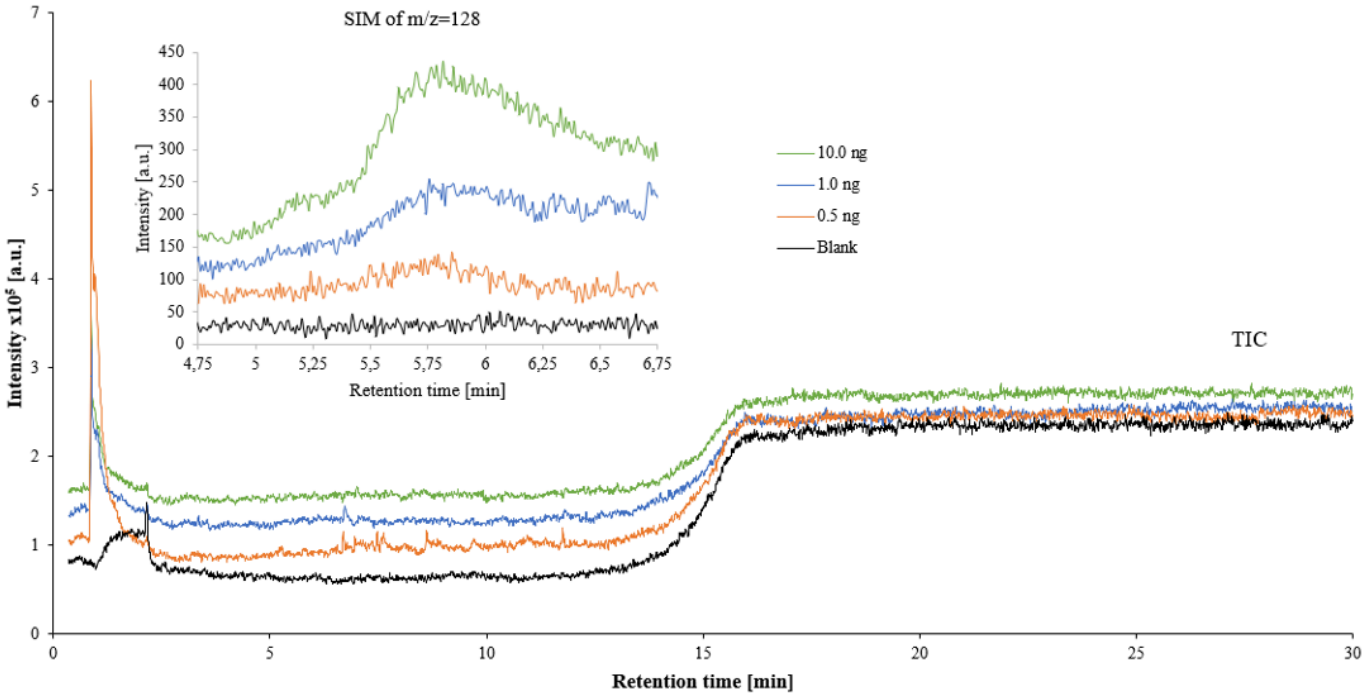


Figure 1

Schematic Pyrograms of PVC

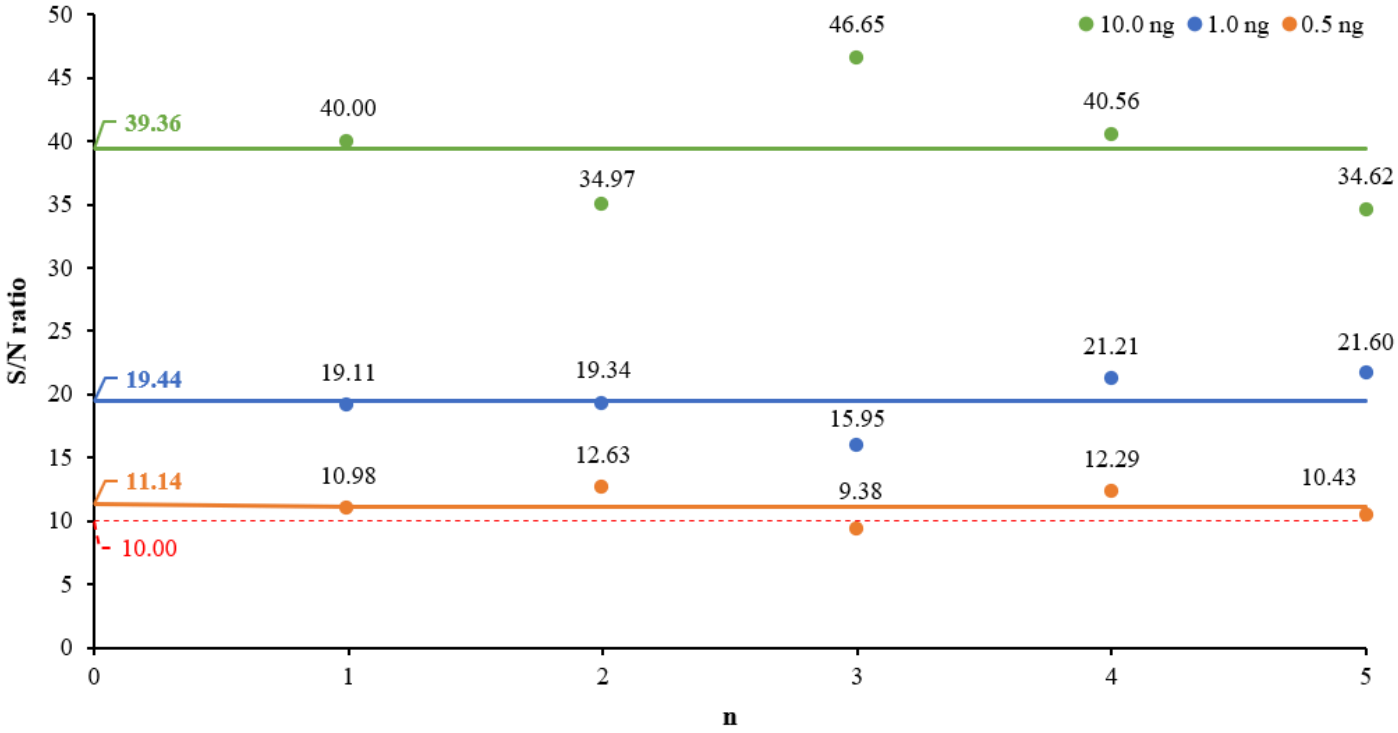


Figure 2

S/N ratio chart for PVC measurements

Supplementary Files

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- Supplementarymaterial.docx