



Quantitative analysis of unstable gas components using GC-PDD

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1. Introduction

We analyze various gaseous impurities in our product gases using gas chromatographs as part of our quality assurance of industrial gases we produce. Gas chromatographs can handle a wide variety of measurement target gases and impurity components through appropriate selection of columns for separating components in gases and detectors for detecting each component. This paper presents our efforts to expand the range of analyzable impurity components of gas chromatograph-pulse discharge detectors (GC-PDDs), which are capable of analyzing a variety of impurity components in the order of parts per billion (ppb).

We have conventionally used GC-PDDs to analyze oxygen and other air components, as well as hydrocarbons. However, in recent years, there have been diversifying requirements from users for quality assurance, and the assurance of unstable components is required in the growing number of cases. Quantitative analysis using a GC-PDD requires a calibration curve created by using a standard gas, and it has been difficult to analyze unstable components for which the production of a standard gas is difficult. Against this background, we have developed a method for quantitative analysis of unstable gas components using a GC-PDD by creating a calibration curve using stable alternative gas components (hereinafter referred to as stable standard components).

2. GC-PDD

2-1 Principle of GC-PDD

A GC-PDD consists of a chromatogram section that time-separates multiple components and a detection section that measures the intensity of each component. The detector is based on pulse discharge detection and generally uses helium (He) gas as the discharge gas. He gas introduced into the discharge area of the detector is excited by pulse discharge to He₂^{*}, and emits light with a wavelength of 70 to 90 nm at the time of its return to the ground state of He. The photon energy released in this process is 1301 to 1701 kJ/mol. The GC-PDD,

in which gaseous impurity components with ionization energies lower than this photon energy are ionized, collects the electrons generated by ionization using a bias electrode to a collection electrode, amplifies this current with an electron multiplier tube, and measures and calculates it to detect the amount of ionized gaseous impurity components (Figure 1 and Figure 2). In other words, GC-PDDs detect the concentration of the measurement target component as an intensity based on the difference (ΔIE) between the light energy obtained by He emission and the ionization energy of the component to be analyzed.

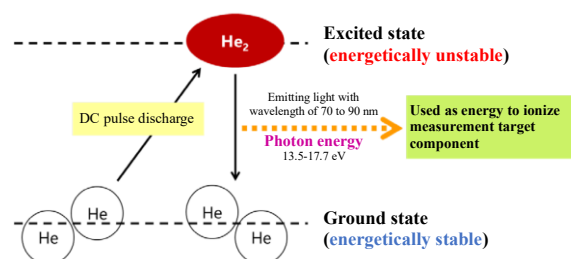


Figure 1 Principle of photon energy generation using pulse discharge

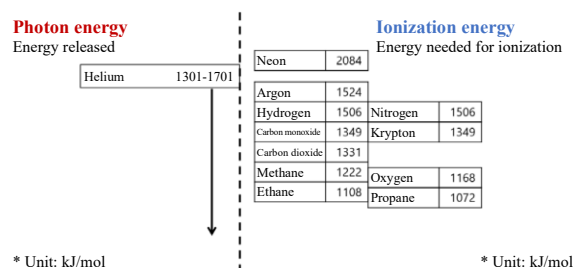


Figure 2 Light energy of He and ionization energies of various gas components ¹⁾

2-2 Example of analysis using GC-PDD

As described in Chapter 1, we quantitative-analyze gaseous impurities in our product gases using a GC-PDD based on a calibration curve created by using a standard gas. Figure 3 shows a calibration curve for methane (CH₄) as an example. The horizontal axis represents the concentration of CH₄ in the gas introduced into the GC-PDD, and the vertical axis represents the integral value of the electrical signal

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detected by the GC-PDD (hereinafter referred to as peak area). The calibration curve exhibits a quadratic function, indicating that the accuracy of the concentration of CH₄ in the standard gas is very important. Since hydrocarbons such as CH₄, ethane (C₂H₆), propane (C₃H₈), benzene (C₆H₆), toluene (C₆H₅-CH₃), and styrene (C₆H₅-CHCHCH₂) are stable in the steady state, the production of standard gases, i.e., the creation of calibration curves, can be performed appropriately, enabling analysis with high accuracy.

ΔIE varies depending on the component as described in Section 2-1, and also so does the peak area. Figure 4 shows the relationship between the peak area and ΔIE obtained from GC-PDD analysis of a standard gas (base gas: He) containing 100 ppm of the above six components. It is observed that both peak area and ΔIE increase as the molecular weight increases, and that there is a high correlation between the peak area and ΔIE.

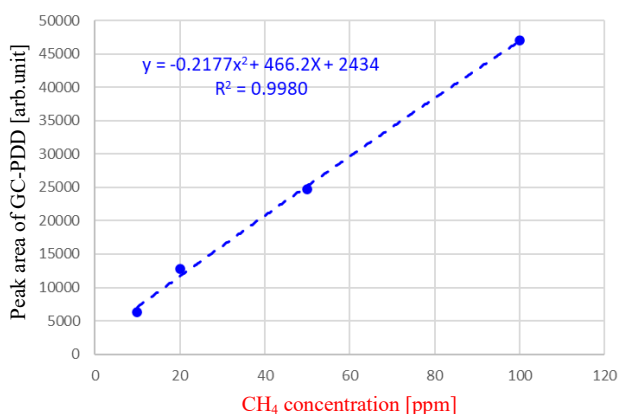


Figure 3 Calibration curve between CH₄ concentration and peak area

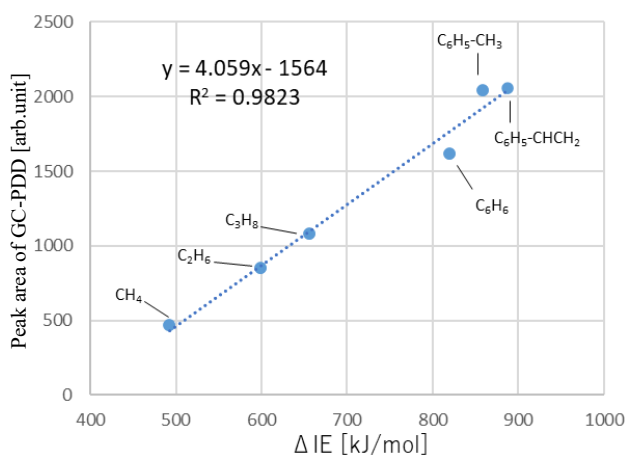


Figure 4 Relationship between ΔIE of stable standard component and peak area per ppm measured by GC-PDD

3. Analysis of unstable gas components using GC-PDD

One of the unstable components the analysis of which has been requested in recent years is tetrafluoroethylene (C₂F₄). C₂F₄ is a raw material for synthesis of polytetrafluoroethylene (PTFE), and is known to be generated when PTFE is irradiated by laser light²⁾. It is also known that octafluorocyclobutane (C₄F₈), one of the perfluorocarbons, is a stable gas component known as a greenhouse gas, but it decomposes to C₂F₄ when high energy is applied³⁾.

3-1 Estimation of ionization energy of unstable gas components

The ionization energy of C₂F₄ is known to be 978 ± 6.8 kJ/mol⁴⁾ (ΔIE = 729 ± 6.8 kJ), which includes some variation. This is not only because it is difficult to create the standard gas due to its instability, but also because it is difficult to suppress the variation in the evaluation experiment of ionization energy. Therefore, we attempted to calculate the ionization energies of unstable gas components using simulations.

Specifically, this calculation used the quantum mechanical calculation method with "B3LYP" as the density functional theory method and "cc-pVDZ" as the basis function. The ionization energies of the stable standard component and the unstable gas component were calculated by calculating the enthalpy of the ground state structure (enthalpy when the charge is 0) and the enthalpy of the positively charged structure (enthalpy when the charge is +1) and subtracting the former from the latter.

First, the photon energy of He was calculated to be 1701 kJ/mol. Next, the ΔIEs of the six stable standard components mentioned in Section 2-2 were calculated. As a result, a high correlation was observed between the literature values and the calculated ΔIEs, as shown in Figure 5, confirming the validity of the ionization energy estimated by the simulation. The ΔIE of C₂F₄ calculated by the simulation was 784 kJ/mol, which is closer to the calibration curve of the candidate stable standard component than the ΔIE literature value of C₂F₄ and is plotted close to C₆H₆.

As described above, it was indicated that this simulation can be used to estimate the ΔIE of the unstable component, for which no literature values are available.

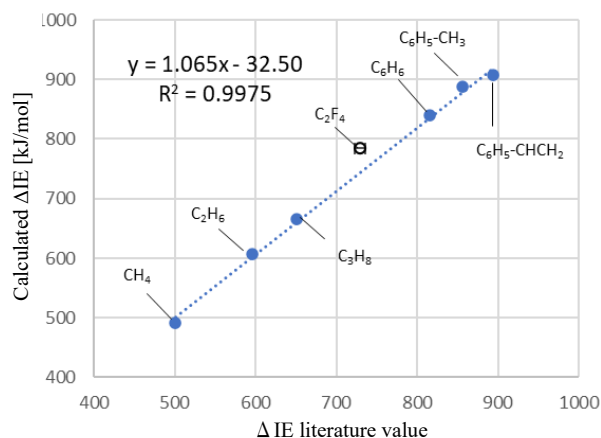


Figure 5 Relationship between calculated ionization energies of stable standard components and C₂F₄ and their literature values

3-2 Creation of calibration curve of C₂F₄ using stable standard components

As described in section 3-1, the ΔIE of C₂F₄ calculated by the simulation is close to C₆H₆. Therefore, we created a calibration curve of C₂F₄ by creating a calibration curve of the concentration and peak area of the calculated ΔIE of C₆H₆ (839 kJ/mol) and correcting the peak area using the ratio of the ΔIEs of both components (Figure 6).

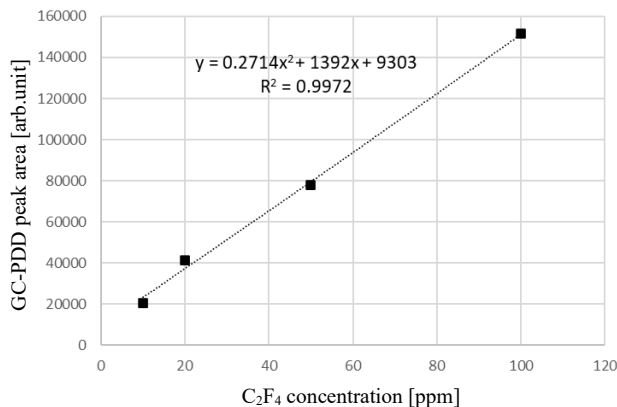


Figure 6 Calibration curve of C₂F₄ created by using C₆H₆ standard gas

4. Conclusion

In order to expand the range of analyzable components of GC-PDDs, we proposed a calibration curve creation method (following three steps) for unstable gas components, the standard gases of which are difficult to produce.

1. Calculate ΔIEs of unstable gas components and stable standard components by using the quantum chemical calculation method.
2. Create a calibration curve of the stable standard component

using the standard gas of the stable standard component

3. Create a calibration curve of the unstable gas component by performing correction with the ratio between ΔIEs of both components.

This paper explained the ΔIE calculation method, its validity, and the calibration curve generation method using C₂F₄ decomposed and generated from PTFE and C₄F₈ as the unstable gas component and hydrocarbon gases such as C₆H₆ as the stable standard component, and it was determined that this technology can be applied also to other gases than C₂F₄.

In the future, we plan to verify the accuracy of calibration curves created by using this technology and to study applicable gas components.

Reference

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