Overview of Precious Metal Content Analysis Methods in Automotive Catalytic Converter

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Abstract

With the increasing awareness of environmental protection, people's concern of pollution issues arising. Vehicles, as the most important means of transportation, its exhaust emission has received considerable attention. The catalytic converter is able to purify harmful substances in exhaust gas. The absolute content of precious metals in the catalytic converter dominates the exhaust gas purification effect. Accurate detection of precious metal content is of great significance for controlling the cost of catalysts, ensuring catalytic performance and recovering precious metals from spent catalysts. We herein summarized several instruments for precious metals content exploration, such as X-ray fluorescence spectrometer (XRF), atomic absorption spectrometer (AAS), inductively coupled plasma emission spectrometer (ICP) and spectrophotometer. In this thesis, the feasibility of using various devices for characterizing precious metal content in catalytic converters is analyzed and their strengths or weaknesses are elaborated.

Keywords

Catalytic Converter, Precious Metal Content, Analysis Methods

1. Introduction

New emission standard was implemented in China on July 1, 2023, the vehicles that do not meet the standard are prohibited sold, imported and produced. The standard placed higher rules on the exhaust emission of vehicles, thus tighter requirements have been put forward for automotive exhaust treatment devices. Automotive exhaust contains large amounts of harmful gases such as carbon monoxide (CO), hydrocarbons (HC), and nitrogen oxides (NO_x) [1] [2] [3] [4].

The harmful gases in the exhaust gas can be partially converted into harmless gases after being treated by the catalytic converter, as the precious metals in the converter play a decisive role [5]. Most precious metals have high activity in CO oxidation. Particularly, platinum (Pt) and palladium (Pd) present high oxidation reaction activity in HC. Rhodium (Rh) plays an excellent role in controlling NO. Thus, catalyst composed of Pt, Pd and Rh is the prime choice for purifying automotive exhaust gases [6] [7]. Significantly, the content of precious metals determines the effectiveness of tail gas purification in whole exhaust emission devices [8] [9]. Sensitive and accurate testing the precious metals contents is the critical issue in the field of analytical sciences.

A national standard on precious metal content determination has been released in China since 2009, which provides the specific detection process of spectrophotometry. With the development of technology for measuring precious metals, many advanced instruments have been investigated. For example, X-ray fluorescence spectrometer (XRF), inductively coupled plasma emission spectrometer (ICP) and atomic absorption spectrometer (AAS) all demonstrated high accuracy in testing precious metal content.

2. Testing Methods

The determination process of precious metal content in catalytic converter generally includes a pre-treatment step, after which the specific content measurement is carried out. The pre-treatment process includes acid dissolution, alkali dissolution, and co-precipitation. The main function of the hydrochloric acid immersion step is to dissolve the carrier of the catalytic converter, the Pt, Pd, and Rh in the converter maintain the initial state in the acid solution. Then, fuse the residue with the mixture of sodium peroxide and sodium hydroxide at high temperatures, acidified with the strong acid solution. After that, adding tellurium to precipitate precious metals. Pt, Pd and Rh powders are obtained after filtration. Subsequently, the elemental content of three precious metals is determined by AAS or ICP. The exploration of the specific determination process and principle are presented below.

2.1. Spectrophotometry

The spectrophotometer, as the common instrument for analysis, is able to determine the absorption of the material to the monochromatic radiation, thus defining the content of the substance in the solution. Spectrophotometer is of high sensitivity and accuracy, which can simultaneously determine the contents of various substance components in the aqueous sample [10]. The specific experimental process is shown in Figure 1.

The sample is heated and dissolved in HCl and H_2O_2 in polytetrafluoroethylene autoclave, then transfer the mixture to oven and heat at 150˚C. Next, adding dibenzyl dithiooxamide (DbDO), KI and Vitamin C (Vc), measuring Pt and Pd contents with a double-wavelength spectrophotometer; KI, 2-mercaptobenzimidazole
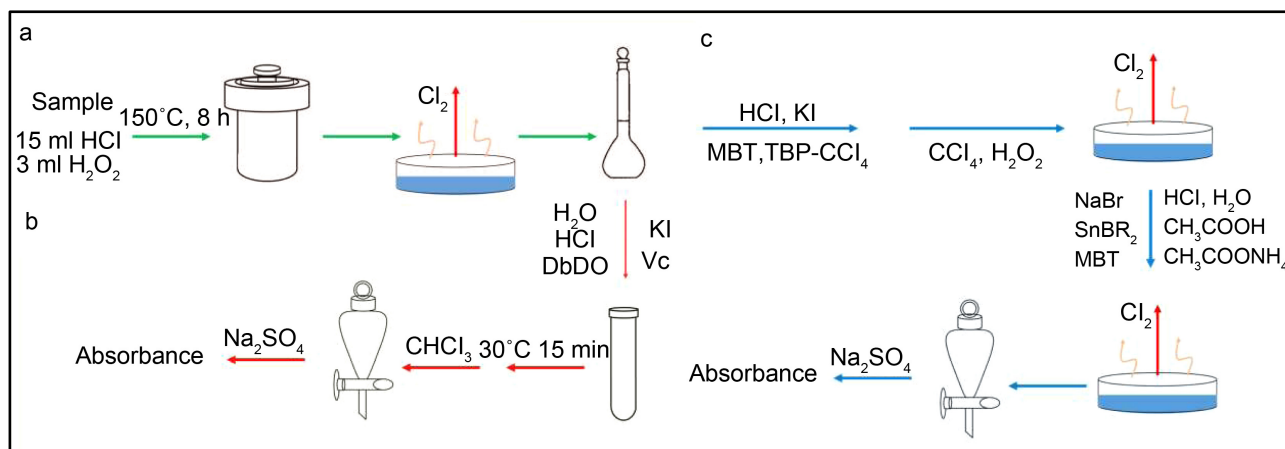
Figure 1. (a) Preparation of sample solution; (b) Determination of Pt and Pd; (c) Determination of Rh.

(MBT) and TBP-CCl$_4$ are employed in order in the process of extraction separation Pt and Pd. The content of Rh in the sample solution is analyzed by extraction spectrophotometry with 2-mercaptobenzimidazole-SnBr$_2$ reagent.

Spectrophotometer is an advanced analysis instrument with excellent accuracy. Moreover, spectrophotometer testing is relatively inexpensive. However, the application of spectrophotometer requires consideration. For example, the testing process of the spectrometer involves the oxidation-reduction of chemical agents, which will definitely generate sewage. The disposal of the sewage is really cumbersome and expensive. Besides, the operation of spectrophotometer is difficult and the concentration of the sample to be measured is determined by the actual situation, proficient use requires extensive training and practice. Therefore, it is necessary to comprehensive consider whether spectrophotometer is indispensable based on actual needs.

2.2. Atomic Absorption Spectrometry

AAS can also quantify precious metal content in sample. The ground state atomic vapor of the pilot sample will absorb the characteristic radiation emitted by the illuminant. The characteristic spectral line intensity weakened after being absorbed by the pilot sample, the decline degree of spectra intensity is defined as absorbance (A), the absorbance is proportional to the content of the pilot element, which law follows the Equation:

$$A = KC$$

K represents a constant, and C is the concentration of the sample solution. Various elements with different atomic structures and outer electrons arrangement will adsorb energy when migrating from the ground state to the first excited state, the resonance absorption lines of each element present different characteristics. The law provides elements qualitative basis, and the intensity of absorbed radiation is defined as quantification basis.

The methods of AAS are divided into the atomic absorption flame method and the atomic absorption graphite furnace method. The atomic absorption flame me-

thod can identify the sample concentration at ppm level. As shown in **Figure 2**, with the high temperature of flame, the molecules in the sample convert into atoms, the content of the sample is confirmed by measuring the absorption degree of specific wavelengths of light. The flame atomic absorption method is easy to operate and relatively inexpensive, which is suitable for large number samples rapid analysis. But the flame atomic absorption method is slightly inferior in sensitivity and accuracy, compared to the graphite furnace atomic absorption method.

The atomic absorption graphite furnace method can discern the sample concentration at the ppb level. Different from the atomic absorption flame method, during atomic absorption graphite furnace method process, the sample is first dissolved and sprayed into graphite tube, dried and pyrolyzed at high temperature. Then, the element content is measured by quantifying the absorption of the light with a specific wavelength. Compared to other methods, AAS has the superiority of high detection sensitivity and high accuracy, which is suitable for quantitative analysis [11] [12]. However, its application is hindered by difficult operations and expensive costs. Besides, AAS requires not less than 10 ml of non-toxic sample, and the mutual interference between precious metal elements cannot be ignored. Buffer agents are usually added to overcome the impact caused by metal ions. AAS has become the most widely application for Pt, Pd and Rh quantitative analysis, which show the ability to analyze trace components on precious metal content in catalyst samples.

2.3. Inductive Coupled Plasma Emission Spectrometry

As a precision instrument, ICP has been reported in numerous articles and standards on measuring the content of precious metals in converter or alloy. The ICP method is composed of the inductively coupled plasma atomic emission spectrometry (ICP-OES) method and inductively coupled plasma atomic emission mass spectrometry (ICP-MS) method, both of their tests rely on the generated inductively coupled plasma [13] [14].
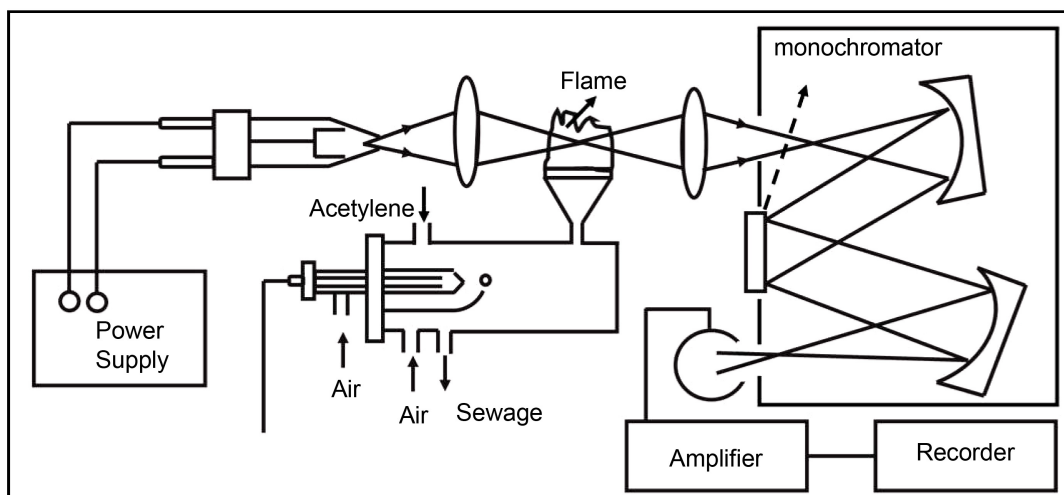

Figure 2. Schematic diagram of the structure of AAS.

2.3.1. ICP-MS

Prior to the cations entering the mass spectrometer, the sample is completely evaporated, dissociated, atomized and ionized when ICP-MS works. The mass spectrometer performs separation, qualitative and quantitative analysis based on the proportion of cation mass and charge (**Figure 3(a)**). ICP-MS is superior in sensitivity, selectivity, and isotope analysis, which has significant advantages for analyzing trace elements and isotopes, ICP-OES is more expert in multi-element analysis and qualitative analysis, which is suitable for analyzing sample composition.

2.3.2. ICP-OES

The operational process of ICP-MS is complicated, while ICP-OES is automated, operators can conduct testing according to standard methods. The detection process of ICP-OES is shown in **Figure 3(b)**.

First, the sample after atomization is transferred into axial plasma channel. Under the insert gas condition, the atomized sample is completely evaporated, atomized, ionized, and excited. And then, the characteristic spectral lines of the emitted elements in sample entered the spectral detector after being identified by spectroscopic system. Finally, the spectral detector conducts qualitative and quantitative analysis based on the characteristic spectra of the elements. The accurate data can be drawn as the response value on the element characteristic spectrum (the value is proportional to its concentration).

With the element concentration value as the horizontal axis, and the element response value or the ratio of the element response value and internal standard element response value as the vertical axis, drawing the standard curve. Then, analyze the concentration of the test solution and calculate the contents of Pt, Pd and Rh according to the follow Equation:

$$\rho i = \frac{10^{-6} \times \rho i' \times v \times S \times m}{W \times V}$$

ρi and $\rho i'$ represent the content of each precious metal element and the measured element in the test solution on the carrier of the catalytic converter, $i =$ Pt, Pd and Rh. v and W represent the constant volume and mass of the sample. S
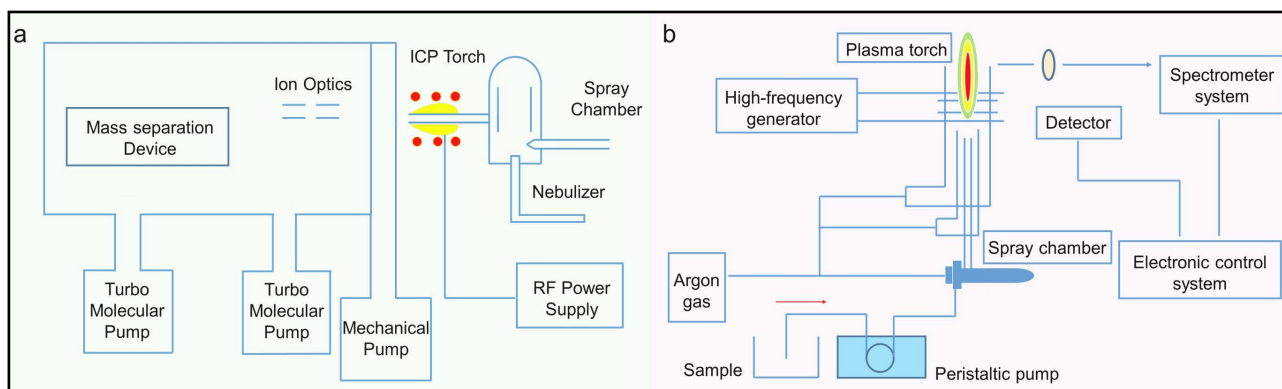

Figure 3. (a) Detection process of (a) ICP-MS and (b) ICP-OES.

represents the dilution ratio. *m* and *V* represent the mass and volume of the catalytic converter carrier.

ICP testing performs low detection limits. However, the operating cost of ICP is high and various factors can influence ICP results. ICP also requires the sample to be non-toxic and non-explosive, with a sample mass of more than 0.1 g. These all increase the difficulty of its actual operation.

2.4. X-Ray Fluorescence Spectrometry

XRF is one of the most convenient instruments for conducting elemental analysis, which works by the interaction between X-rays and substances [15]. When the light source illuminates, the high-energy rays react with atoms. If the energy exceeds or equals the binding energy of electrons in atom orbital, electrons in the orbital are expelled and form holes, which leads the atom state to become unstable. As a result, the outer electrons of the orbit are removed from the holes, ensuring the atom is back in a stable state. During the outer electrons transition process, the energy difference between shells is emitted in the form of X-rays, generating the characteristic X-ray fluorescence. The fluorescence X-rays of various elements present specific wavelengths, and the composition of the elements is determined based on the fluorescence captured by the detector (**Figure 4**).

In addition to qualitative analysis, XRF performs quantitative analysis with reliable reference material. The quantitative methods of XRF include standard curve method, incremental method, internal standard method, etc. However, no matter which method is employed, we all need to use a standard sample to determine the standard curve. Furthermore, the compositions of the standard sample and the sample to be tested should at similar concentration level. XRF is non-destructive testing, which can analyze the content of multiple elements simultaneously [16]. XRF can perform the sample with a concentration above 1 mg/kg. However, XRF has certain shortcomings. XRF can only analyze the surface layer of the sample. For the samples with higher thickness, surface treatment or cutting is
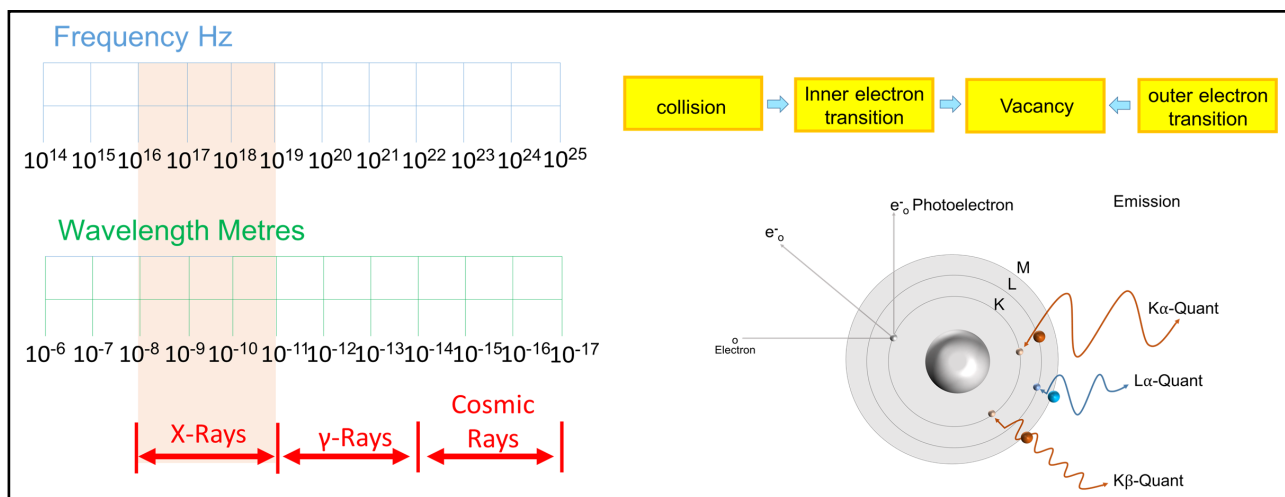

Figure 4. Schematic diagram of characteristic spectrum generation.

required. Besides, the samples should be flat and uniform, which is favorable to X-ray irradiation and fluorescence signal reception.

With the merits of technology, the detection accuracy of instruments greatly improved. More and more methods can be used to detect the content of precious metals Pt, Pd and Rh in catalytic converters. For example, oscillographic polarography can also measure Pt, Pd and Rh after calibrating the standard curve. In practical applications, selecting the appropriate method under appropriate conditions is the key to accurate detection.

3. Conclusion

The precious metal content detection plays a crucial role in cost control and exhaust treatment. This article reviews the detection methods and their usage conditions, providing a new perspective for precious metal detection.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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