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# Miniaturized dielectric barrier discharge–atomic emission spectrometer for pesticide: Sensitive determination of thiram after derivatization with mercurial ion

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ABSTRACT

A novel method was developed to sensitively determine thiram (which we selected as a representative large molecular organic pesticide) using miniaturized dielectric barrier discharge-atomic emission spectrometry (DBD-AES), based on the determination of free mercurial ion ($Hg^{2+}$) from Hg labeled thiram complex. The disulfide bond (—S—S—) in thiram was reduced to sulfhydryl (—SH) using *tris*(2-carboxyethyl)phosphine (TCEP), and inorganic $Hg^{2+}$ was used as the derivatization reagent. It was found that $SnCl_2$ could selectively reduce only free $Hg^{2+}$ to $Hg^0$ vapor in the presence of $Hg^{2+}$-labeled thiram complex, which could be separated from sample matrices for sensitive DBD-AES detection. Under the optimized conditions, this method provided high sensitivity for thiram determination, with limits of detection as low as 0.0003 mg $kg^{-1}$ and linear dynamic ranges of 0.001–0.01 mg $kg^{-1}$. This analytical method performs better than the traditional analytical methods, demonstrating the potential usefulness and versatility of this new Hg-labeled DBD-AES system.



## 1. Introduction

Pesticide residues have raised serious concerns because of harmful effects on the environment and human health. Although traditional GC/LC-MS (gas/liquid chromatography–mass spectrometry) techniques in laboratory are relatively mature for determining most pesticides in real samples, miniaturized instruments are attracting increasing attention for detection of pesticide residues in the field. In the last decade, many new techniques have been successfully used for the detection, including the use of surface-enhanced Raman spectroscopy [1], fluorescent probes [2], luminescence [3], infrared spectrometry [4], and electrochemiluminescence sensors [5]. However, detection of pesticide residues in the field is still challenging because the traditional methods tend to be influenced by the stability and selectivity of the methods. Moreover, these methods require bulky and expensive instruments and they consume large power. However, atomic emission spectroscopy (AES) with high stability and selectivity has recently been successfully used for the determination of pesticides [6]. The traditional benchtop AES instruments are usually bulky and expensive and consume large power [7,8]; they are also not portable, making the detection of pesticide residues in the field difficult. Therefore, microplasma, which offers important advantages of a simpler setup, lower power and gas consumption, field-portability, and convenient operation, has been extensively applied in various fields of analytical atomic spectrometry [9–12].

Dielectric barrier discharge (DBD), a kind of microplasma, forms by electric discharge between two electrodes separated by an insulating dielectric barrier [13]. Since Franzke et al. [14] first used DBD for the atomization of halogenated hydrocarbons for diode laser atomic absorption spectrometry and Zhang et al. [15] pioneered DBD's applications in traditional atomic spectrometry, DBD has now been widely used in analytical spectrometry as an atomizer to generate chemical vapors [16], as well as in molecular emission spectrometry [17–19], atomic fluorescence spectrometry [20], and as an ionizer for mass spectrometry [21]. For atomic emission spectrometry (AES), Yu et al. [22] and Zhu et al. [23] first determined Hg using DBD as the excitation source. In our previous work, we used DBD microplasma to excite the carbon atomic emission [24]. However, further application of DBD in AES is limited by the weak atomization/excitation capability deriving from its low power consumption confines [25]. The miniature AES-based DBD microplasma is not suitable for the determination of large molecular organic compounds such as pesticide.

Pesticides usually can be classified based on their chemical structures such as carbamates, organochlorides, organophosphates, and organosulfur [26]. It is very difficult to directly excite all these pesticides by the DBD microplasma, owing to its low excitation capability. In

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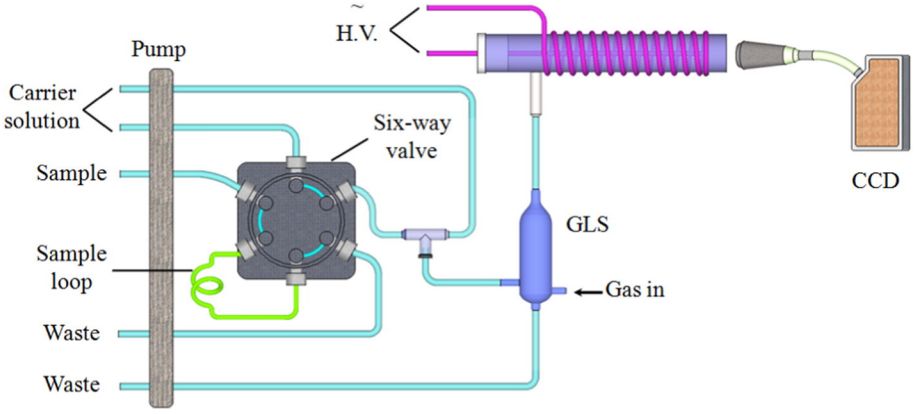


**Fig. 1.** Schematic of the flow injection DBD-AES system for thiram.

recent years, metal-labeling strategy has become popular for the analysis of various proteins [27] and different tissues [28]. Using this strategy, Wang et al. [29] and Mester et al. [30] successfully quantified compounds containing sulfhydryl (—SH) and disulfide bond (—S—S—) using Hg as the labeling element. Therefore, it can be surmised that organosulfur pesticides labeled with Hg should be excited by DBD microplasma to determine the pesticide content [31].

In this work, we present a simple DBD-AES system for determining the presence of disulfide bond-containing pesticides in various food samples. Thiram (bis-(dimethyldithiocarbamoyl) disulfide), a dithiocarbamate pesticide, was selected as the organosulfur compound containing disulfide bond [32]. Inorganic mercury ($Hg^{2+}$) was chosen as the derivatization reagent to label the thiram. Because disulfide bond cannot be derivatized with $Hg^{2+}$ directly, *tris*-(2-carboxyethyl)-phosphine (TCEP) was used as the reducing reagent to reduce the disulfide bond to free sulfhydryl. When the $SnCl_2$/HCl reducing system is used, the Hg-labeled thiram cannot be reduced to $Hg^0$ vapor to transfer into the DBD microplasma, which decreased the signal of Hg in the DBD-AES system. Then, the thiram in the sample could be detected with high selectivity. In particular, once the concentration of $Hg^{2+}$ corresponding to the maximum residue limits (MRL) was used to label the thiram, it would be convenient to distinguish directly whether the thiram concentration in the sample exceeds that of the MRL. To the best of our knowledge, this is the first report for pesticide residue analysis on the use of a AES system.

## 2. Experimental section

### 2.1. Reagents

High-purity 18.2 MΩ cm ultrapure water was produced by a Milli-Q water purification system (Millipore, USA). The stock solution of inorganic mercury ($Hg^{2+}$; 1000 mg $L^{-1}$) was purchased from the National Research Center for Standard Materials (NRCSM, China, Beijing). TCEP (*tris*-(2-carboxyethyl)-phosphine) was purchased from Sigma-Aldrich (St. Louis, MO, USA). High-purity chemicals (ethylenediaminetetraacetic acid (EDTA), NaOH, $SnCl_2$, and HCl) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Solid standard powder of thiram (chemical formula: $C_6H_{12}N_2S_4$) was purchased from Dr. Ehrenstofer GmbH (Augsburg, Germany).

Thiram was dissolved in 0.2 mol $L^{-1}$ EDTA (pH = 9.6–10) to achieve a concentration of 100 mg $L^{-1}$, which was used as the standard stock solution. Fruit and vegetable samples were purchased from a local market and were stored at −20 °C until analysis.

### 2.2. Instrumentation

Fig. 1 provides a schematic of the flow injection DBD-AES system using $SnCl_2$ as the reductant for the Hg-labeled thiram. The flow injection reactor comprises a four-channel peristaltic pump (BT100-4, Shanghai Huxi Analysis Instrument Factory Co., Ltd., Shanghai, China) for the carrier solution and a six-port injection valve for sample injection. A three-port valve was used to mix the carrier solution ($SnCl_2$) and sample, and the mixture was connected to the gas-liquid separation (GLS) system, wherein an Ar carrier flow was introduced to directly flush the reactant $Hg^0$ gas into the DBD-AES detector.

The miniaturized DBD-AES detector comprised a laboratory-built cylindrical DBD device according to our previous work [33] and a commercial hand-held CCD spectrometer (Maya2000 Pro, Ocean Optics Inc., Dunedin, FL). The DBD device consisted of a quartz tube (50 mm × 3.0 mm i.d. × 5.0 mm o.d.) and two separated copper wires used as electrodes, which were tightly and evenly wrapped around the outside of the tube (1.2 mm in diameter) and inserted into the tube (1.7 mm in diameter), respectively. A high-voltage power supply (CTP-2000K, Nanjing Suman Electronics Co., Ltd., China) was used to connect the

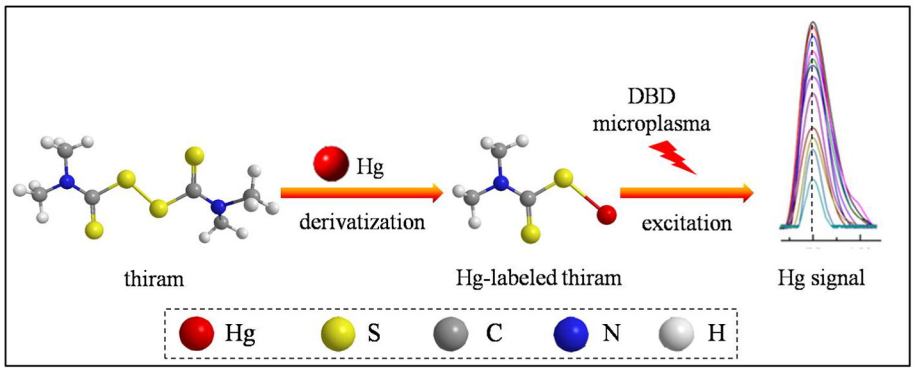


**Fig. 2.** Schematic diagram of the derivatization with Hg and excitation with DBD microplasma for thiram.