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Flow injection-photoinduced-chemiluminescence determination of ziram and zineb

J.L. López Paz, M. Catalá-Icardo*

Integrated Coastal Management Research Institute, Higher Polytechnic School of Gandia, Polytechnic University of Valencia, Carretera de Nazaret-Oliva s/n, Grao de Gandia, 46730 Gandia, Valencia, Spain

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ABSTRACT

A simple, sensitive and rapid method for the determination of the pesticides ziram and zineb was described. This new method was based on the coupling of FIA methodology and direct chemiluminescent detection; this approach had not been used up to now with these pesticides. The additional use of an 'on line' photochemical reaction, which was performed by using a photoreactor consisting of a long piece of PTFE helically coiled around a 15 W low-pressure lamp, increased by a factor >20 the chemiluminometric response of the pesticides. An additional 3-fold improvement in the analytical signal was also achieved by using quinine as sensitizer. The obtained throughputs were very high (121 and 101 h^{-1} for ziram and zineb, respectively); this feature together with its low limit of detection (1 ng mL^{-1}) makes this method particularly well suited to routine analyses of environmental samples. On the other hand, its applicability to two members of the dithiocarbamate family of pesticides, makes it promising for the determination of the rest of the members of this family. The method was demonstrated by application to spiked water samples from different origins (ground, river and irrigation).

1. Introduction

Ziram [Zinc bis (dimethyldithiocarbamate)] and zineb [Zinc ethylene-1,2-bisdithiocarbamate)] (molecular structures in Fig. 1) are broad spectrum fungicides. They are mainly used to prevent crops damage in the field and during their storage or transport because of its low phytoxicity. Ziram is also formulated into a bird and rodent repellents and registered for use as an industrial preservative in exterior latex paints, adhesives, caulking and sealants; zineb is also used in antifouling products. Both belong to the dithiocarbamate group of fungicides which have replaced most of organochlorine pesticides. They have neuropathy as a common toxic effect and direct exposure to them can also cause allergy to skin and inflammation of eyes and respiratory tract in humans [1]. Despite of the acute toxicity for these compounds is low, they were found to be carcinogenic in a pathological study [2]. On the other hand, they can form strong complexes with trace elements such as Cu(II) when are released into the environment; these complexes have been shown to increase trace uptake by aquatic organisms. Moreover, there is growing concern about the potential estrogenic effects and chronic toxicity of these compounds on other animal species [3].

The standard procedure recommended for these substances by the AOAC (Official Methods of Analysis) involves the production of CS_2 by acid hydrolysis, which is absorbed in a methanolic potassium hydroxide solution; the xanthate so formed is then titrated iodimetrically [4]. This method has drawbacks associated with the detection of end point with

* *Corresponding author*. Tel.: +34 963877815; fax: +34 963877809.
E-mail address: jolopa@qim.upv.es (J.L.L. Paz).
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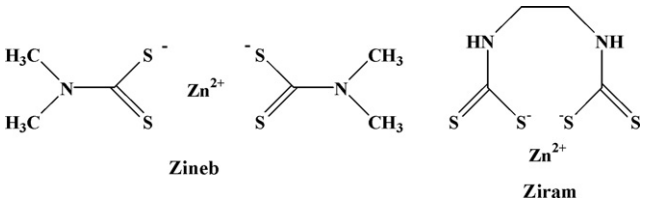

Fig. 1 – Molecular structures of ziram and zineb.

starch, the production of H_2S from sulfide impurities and the hydrolytic decomposition of xanthate solutions.

Many of the recent analytical methods developed up to now for the determination of ziram are spectrophotometric [5–9], but they are time consuming and their sensitivity is low. Gas chromatographic (GC) methods are commonly used for pesticide analysis, but ziram is a non-volatile compound, hence it would not be suitable for direct detection by these methods. Because of this, the GC methods developed for ziram determination are based on detection of CS_2 [10,11]. Some liquid chromatographic (LC) [12–16] methods have been also developed for analysis of pesticides but, despite of its selectivity, they are expensive and involve the use of toxic and expensive solvents. Particularly remarkable, bearing in mind the high number of tested pesticides, is the LC method developed by Yu et al. [17]. These authors were able to analyse 46 analytes out of 52 targets by using a mass spectroscopy detector, however ziram was one of the six for which no result was obtained and zineb was not tested. Other alternative analytical methods such as atomic absorption spectroscopy [6,18–20], capillary electrophoresis [21] and amperometry [22] have been also developed but they are less sensitive than the CL–FIA method herein reported. Moreover some of them require extraction with organic solvents, which is sometimes tedious, time-consuming and prone to errors due to incomplete extraction.

The increasing use of carbamate pesticides have resulted in demands for the development of sensitive and rapid analytical methods. These features are accomplished by the coupling of chemiluminescent (CL) detection and flow injection (FIA) methods. CL systems provide high sensitivities and wide dynamic ranges. On the other hand, FIA techniques allow the rapid and reproducible mixing of sample and reagent near the detector, which makes this methodology particularly well suited to monitoring transient light emission from CL reactions. In addition, the use of light from a low-pressure lamp provides a clean, reproducible and inexpensive "reagent", which offers a powerful means for obtaining derivatives with improved features for analytical methods involving CL-detection. However, although there are many analytical methods for the determination of dithiocarbamate fungicides, to the authors knowledge up to now no method based on CL-photodegradation for ziram and/or zineb has been previously reported. Only one method based on CL–FIA detection has been reported for ziram [23], based on the chemiluminescence produced by the reaction of ziram with luminol in the presence of a catalyst. But this indirect CL method is more complicated and expensive and provided a higher limit of detection than the herein reported direct-CL method.

This paper reports a simple, rapid, sensitive and direct method for the determination of ziram and zineb, requiring no sophisticated equipment and fast enough for use in routine analyses, which are particularly suitable for environmental control. The proposed method is based on CL reaction between the photodegradated pesticides and Ce(IV) in an acidic medium by using quinine as sensitizer. It was successfully applied to the determination of ziram and zineb in water samples from different sources. The present method represent a great financial saving, compared with LC or GC techniques and a much better sensitivity than the reported spectrophotometric methods.

2. Experimental

2.1. Reagents and stock solutions

All experiments were carried out by using analytical reagent grade chemicals and Milli-Q water (Millipore, Bedford, MA, USA). The reagents used were: $KMnO_4$, $K_3Fe(CN)_6$, NaCl, H_3PO_4, acetone, and Triton X-100 from Panreac; HNO_3, $HClO_4$, KIO_4 and $CeSO_4{\cdot}4H_2O$ from Scharlau; H_2SO_4, H_2O_2, ethanol and acetonitrile from Merck; NaOH, HCl, H_2SO_4 and acetic acid from J.T. Baker; β-cyclodextrin, sodium dodecyl sulfate and hexadecylpyridinium chloride from Fluka. Cations tested as potential inorganic interferences were prepared from chloride (Na^+ and K^+ (Panreac), Ca^{2+} (Probus), Mg^{2+} (Prolabo), Zn^{2+} (Scharlau), Mn^{2+} (D'Hernio)) or sulfate (Cu^{2+} (Probus)) salts. Anions were obtained from sodium (NO_2^- (Probus), SO_4^{2-} (Panreac), HCO_3^- (Guinama)) or potassium salts ($H_2PO_4^-$ (Panreac) and NO_3^- (Probus)). Ziram (97.0%) and Zineb (71.50%) were supplied by Dr Ehrenstorfer. The chemicals tested as sensitizers were rhodamine B (Merck), dioxane (Scharlau), 8-hydroxyquinoline (Merck), quinine hydrochloride (Sigma), sodium sulfite anhydrous (Panreac) and acridine orange (Sigma).

100 mg L^{-1} stock solutions of ziram and zineb were prepared in 0.1 M NaOH. In order to remove its impurities, it was necessary to filter zineb solutions by using polyamide membrane filters (0.45 μm) (Sartorius). Both stock solutions were stored at room temperature in the dark. Ziram remained stable for at least 1 month, but the zineb solutions were unstable and hydrolyzed rapidly; because of that it was necessary to prepare them daily.

A 0.001 M Ce(IV) stock solution was prepared from cerium (IV) sulfate tetrahydrate (Scharlau) in 0.01 M sulfuric acid weekly.

A 0.05 M quinine stock solution was prepared from quinine hydrochloride (Sigma) weekly.

The ion exchange resins used for sample treatment were Duolite C206A (Acros organics) (cationic) and IRA-400(OH) (Supelco) (anionic).

2.2. Apparatus

The flow manifold used is depicted in Fig. 2 and consisted of PTFE coil of 0.8 mm i.d.; a Gilson (Worthington, OH, USA),