



Micro-determination of dithiocarbamates in pesticide formulations using voltammetry



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ABSTRACT

The purpose of this work was to develop a reliable method for the micro-determination of dithiocarbamates (mancozeb, maneb, propineb, nabam, $\text{Na}(\text{CH}_3)_2\text{DTC}$, zineb, ziram, ferbam and thiram) in pesticide formulations for agriculture using adsorptive stripping voltammetry (AdSV).

The accuracy of analytical method was valued by analyzing simulate formulation samples prepared by us with known amounts of active ingredients. In addition, the applicability of the AdSV procedure for the analysis of DTCs and EBDTCs in micro-samples was evaluated by estimating its recoveries from spiked commercial formulate samples. The accuracy, valued as recovery percentage ranged between 85% and 97%. The precision ranged from 1.3 to 6.1%.

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1. Introduction

The pesticide formulations are mixtures of active and other substances. Active substances, in our case dithiocarbamates (DTCs) and ethylenebisdithiocarbamates (EBDTCs) are generally chemical compounds that prevents, kills, or repels a pest or acts as a plant regulator, a desiccant, a defoliant, a synergist, or a nitrogen stabilizer. Pesticide formulations are sold in many different products due to difference in chemical and physical properties of the active substances, ability to control the parasite, and simplicity of handling, transport and employ.

In commercial formulates, in addition to the active ingredients, inert substances may aid in the application. Inert can be solvents, carriers, surfactants or other compounds, which are deliberately added.

Dithiocarbamates are organosulfur molecules defined by a general structure $(\text{R}_1\text{R}_2)\text{N}(\text{C}=\text{S})\text{-SX}$, with R alkyl, alkylene, aryl, or similar other groups, and X usually by a metal ion. Dithiocarbamate is also a chelating agent for some metal ions (Fe^{+2} , Mn^{+2} , Cu^{+2} , Na^+ , Zn^{+2} , and Ni^{+2}) to form coordination complexes and to act as a fungicide. Thiram, ziram and ferbam are analogous dialkyl DTCs with differences in R groups and the later two containing different metal ions between their S atoms. The ethylenebisdithiocarbamates are polymeric since their metal ions can bind several molecules to form polymeric complexes. Various examples of EBDTCs are zineb, maneb, mancozeb and propineb.

Discovered in the 1930s, DTCs were used as fungicides for agricultural applications during World War II [1]. DTCs and EBDTCs are the main group of fungicides used to fight about 400 pathogens of more

than 70 plants and are registered in the European states and many other countries [2]. Following the expiry of some patents that restricted the use of several active substances, recently the potential market of pesticide formulates has increased and thereby the number of consumers potentially effected by these chemicals. This makes it very important that controls be put in place for their correct use to ensure safety of the consumers and of the environment.

Exposure to these compounds has been linked with the development of several negative effects on health [3,4]. Recently, a series of novel dithiocarbamates have been designed synthesized and evaluated for their chemotherapeutic activity [5].

The main purpose of this work was to develop a reliable method for the micro-determination of mancozeb, maneb, propineb, nabam, $\text{Na}(\text{CH}_3)_2\text{DTC}$, zineb, ziram, ferbam and thiram in commercial formulates for agriculture because they cannot be readily measured by conventional techniques used in most laboratories.

The most known method, for analysis of dithiocarbamates trace in food and environmental matrices, is based on an acid decomposition of the sample and analysis of evolved CS_2 by spectrophotometric determination, after being absorbed in an ethanol solution, forming a yellow complex with $\text{Cu}(\text{II})$ in the presence of diethanolamine [6,7]. On the other hand, the obtained CS_2 can be quantified by gas chromatography either directly using a headspace method [1] or by liquid–liquid extraction into hexane [8]. These methods are unable to distinguish among various dithiocarbamates since most of them can be degraded to carbon sulfide. Also, the decomposition of EBDTCs can also yield hydrogen sulfide. Many methods for determination of EBDTCs are based on the measurement of the metal of the compounds, and therefore, many of these methods are similar to those for detection of inorganic iron, manganese or zinc. However, these methodologies assure the content of metal but

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cannot evaluate the possible degradation of pesticide molecules and the metals from different origins (e.g. metal salts).

The major negative aspect of these fairly time-consuming and costly methods is their lack of selectivity resulting from the inability to distinguish between individual DTCs and/or EBDTCs. In addition, CS₂ most likely generated by other chemicals contained in the commercial formulations may deliver false positive results in the analysis of samples.

More selective methods for the analysis of DTCs include HPLC approaches. For an example, some authors presented a method based on reversed phase HPLC with a UV detector for the analysis of some dithiocarbamates and DMDC in food [8,9]. Heavy metal salts were transformed into water soluble salts using an alkaline EDTA solution and a methylation step was carried out previous to HPLC analysis [8]. In several cases, L-cysteine to the EDTA solution is added to minimize the interaction of EBDTCs with co-extractives from the sample. The recovery of fortified samples ranged from ca. 60 to 85% [8].

In this paper, we used adsorptive stripping voltammetry (AdSV) to measure the concentrations of DTCs and EBDTCs in commercial formulations. The method was based on the measurements of the anodic current of dithiocarbamic anions [10]. Unlike anodic and cathodic stripping voltammetry, based on an electrolytic preconcentration step, AdSV technique is based on adsorptive accumulation of the analita on the electrode at open circuit with no charge transferred.

The high sensitivity, selectivity, simplicity and versatility of the AdSV can be attributed to the combination of an effective preconcentration step based on non-electrolytic adsorptive accumulation process with an advance measurement procedure.

There are many reports on the application of voltammetry for the determination of metals [11–14] in different matrices, but to the best of our knowledge, to analyze sulfur-containing compounds, voltammetric methods in few cases were used [15,16].

The most important advantage that voltammetric methods offer for analysis of real matrices is the possibility to use them, often, without preliminary complicated separations. Also, it is frequently possible to have advantage of electrometric methods for the analysis of colored materials or samples containing dispersed solid particles. Voltammetric methods have similar selectivity of chromatographic ones, but they are in general faster and can be carried out in turbid solutions.

Voltammetric methods are used for individual and simultaneous determination of analytes.

The history, theoretical background and applications of voltammetry are given in references [17,18].

In this paper we take in account eight active ingredients contained in their commercially available emulsionable formulations, which are widely used in Europe. The following pesticides were selected as test substances: sodium N,N'-ethylene-bis-dithiocarbamate (Nabam), zinc and manganese ethylene-bisdithiocarbamate (Mancozeb); sodium N-methyldithiocarbamate; zinc N,N'-dimethyldithiocarbamate (Ziram), iron N,N'-dimethyldithiocarbamate (Ferbam); zinc propylene bisdithiocarbamate (propineb); and tetramethylthiuram disulfite (Thiram), although the above-mentioned pesticides have been on the market for many years.

2. Experimental

2.1. Reagents

Crystalline nabam, mancozeb, ziram, ferbam, sodium N-methyldithiocarbamate, propineb and thiram were purchased from Fluka (Milano, Italy). The diluted standard solutions were prepared daily. The reagents used throughout were analytical grade (Carlo Erba, Milano, Italy) and aqueous solutions were prepared in Milli-Q water.

All the prepared stock solutions were stored at 4 °C before use. All electrochemical measurements were conducted in a 0.05 M acetate buffer, pH 5 (Carlo Erba, Milano (Italy)).

2.2. Preparation of the samples

Due to the extremely low solubility of investigated active ingredients in common solvents employed for analysis, also including polar ones such as water or alcohol, these compounds cannot be easily analyzed in water and it is necessary to treat the solid samples with an appropriate reactive.

In particular, mancozeb, maneb, propineb, nabam, Na(CH₃)₂DTC and zineb were solubilized in water in the presence of high concentration of chelating agents such as sodium salt of EDTA while ziram and thiram were solubilized in acetone. Ferbam was solubilized in sodium phosphate.

2.3. Preparation of solutions (extraction)

An accurate weight of the order of 10 mg of the sample (simulate or commercial formulate) (Table 1) was placed into an Erlenmeyer flask and treated for 15 min by sonication with 15 mL of the appropriate reagent. In particular, formulates containing mancozeb, maneb (n°1), propineb (n°2), nabam (n°4), Na(CH₃)₂DTC (n°5) and zineb (n°8) were treated with a 0.1 M solution of Na₂EDTA, ziram (n°3) and thiram (n°9) with acetone and ferbam (n°6) with a 0.1 M solution of Na₂HPO₄. In the case of formulations n°10, n°11 and n°12 containing ziram, ferbam and thiram, it was not possible to perform the analysis in acetone, as expected from the initial solubility tests, since in these conditions, was solubilized a fraction of the sulfur of the formulation that produces a signal between –0.40 and –0.50 V which overlaps the characteristic peak of the analytes, thus not allowing the determination. In this case we repeated the analysis in different conditions and precisely treating the formulates containing ziram and ferbam respectively with a large excess of EDTA and Na₂HPO₄. Only in the case of the formulation n°12, containing thiram and sulfur, we have not obtained satisfactory results, being the thiram an active substance metal-free and soluble in acetone.

On the other hand, for the sodium dimethyldithiocarbamate, structurally similar to ferbam, we have not revealed anomalies of this kind because sulfur is not soluble in EDTA, and is then removed by centrifugation.

The resulting suspension was centrifuged, the residue was washed twice with the same solution or reactive utilized for the solubilization, and the clear solution was transferred into a volumetric flask and brought to volume.

2.4. Analytical method

In a preliminary stage of this work, two voltammetric techniques were tested in order to identify the most reliable, in particular, we compared the results obtained, analyzing some DTCs and EBDTCs, with the differential pulse (DPV) and adsorptive stripping voltammetry (AdSV). The best detection limits of the technique in stripping obtained for the compounds in question led us to prefer this method. In this case, electro-active species are accumulated at the electrode surface at a non-defined potential value. Beginning studies were carried out to identify the voltammetric peaks of different pure active substances by following the AdSV voltammograms of solutions containing one active ingredient. As examples, in Figs. 1–4 are shown voltammograms of four active ingredients. From the acquired voltammograms, it can be observed that every analita of the class of EBDTCs gives only a characteristic stripping peak between –0.30 and –0.40 V while every DTC compounds show three peaks between –0.35 and –0.65 V. In particular, nabam (Fig. 1), which is a non-ethylene polymer, shows a behavior more similar to that of polymeric EBDTCs; similarly, the signal relating to the sodium N-N'-dimethyldithiocarbamate (Fig. 2) is more similar to that of the corresponding polymeric DMDCs. From the voltammetric trend of the thiram (Fig. 3), structurally different from the others, it is not clearly discernible.

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