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Salting-out assisted liquid–liquid extraction with the aid of experimental design for determination of benzimidazole fungicides in high salinity samples by high-performance liquid chromatography

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ABSTRACT

A novel method for the simultaneous separation and determination of four benzimidazole fungicides (*i.e.*, carbendazim, fuberidazole, thiophanate-methyl and thiophanate) in high salinity samples was developed by using salting-out assisted liquid–liquid extraction (SALLE) *via* water-miscible acetonitrile as the extractant coupled with high-performance liquid chromatography. Box–Behnken design and response surface were employed to assist the optimization of SALLE conditions, including volume of salting-out solvent, the pH of sample solution and salting-out solvent as variable factors. The optimal salting-out parameters were obtained as follows: 2 mL of acetonitrile was added to 2 mL of sample solution with pH=4 and then 2 mL salting-out solvent containing 5 mol L⁻¹ sodium chloride at a pH of 7 was added to the solution for extraction. This procedure afforded a convenient and cost-saving operation with good cleanup ability for the benzimidazole fungicides, such as good linear relationships ($R > 0.996$) between peak area and concentration from 2.5 ng mL⁻¹ to 500 ng mL⁻¹, low limits of detection between 0.14 ng mL⁻¹ and 0.38 ng mL⁻¹ and the intra-day precisions of retention time below 1.0%. The method recoveries obtained at fortified three concentrations for three seawater samples ranged from 60.4% to 99.1%. The simple, rapid and eco-benign SALLE based method proved potentially applicable for trace benzimidazole fungicides analysis in high salinity samples.

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1. Introduction

Benzimidazole fungicides are used worldwide as broad spectrum pesticides against insects, fungi and weeds on a wide variety of fruits, vegetables and other crops [1,2]. Although many public benefits have been realized by utilizing benzimidazole fungicides, their massive use in the last years has led into their accumulation in the environment, thus contaminating the water streams which cannot be disregarded. European Water Framework Directive has

established a maximum concentration level (MCL) of 0.1 µg L⁻¹ for most benzimidazole fungicides present in natural waters, and a total concentration of all pesticides of 0.5 µg L⁻¹ [3].

Because of widespread use and possible health effects, it is desirable to monitor benzimidazole fungicides in the environment. The low vapor pressure and the thermal instability of benzimidazole fungicides do not permit their direct analysis by gas chromatography unless they are derived into thermally stable derivatives. So the commonly used analytical techniques for benzimidazole fungicides are high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE) coupled with ultraviolet (UV), fluorescence detection or mass spectrometry [4–9].

However, analytes extraction and sample pretreatment are the most challenging and time-consuming steps for a whole analytical process. In all the above work, many extraction methods such as molecularly imprinted solid phase extraction (MISPE) [4–6], dispersive liquid–liquid microextraction (DLLME) [7] and hollow fibre-based liquid phase microextraction (HF-LPME) [8] have been used. Most of these methods are often complicated and time spending,

Abbreviations: ACN, acetonitrile; CBZ, carbendazim; CE, capillary electrophoresis; DLLME, dispersive liquid–liquid microextraction; DMSO, dimethylsulfoxide; FBZ, fuberidazole; HF-LPME, hollow fiber-based liquid phase microextraction; HPLC, high-performance liquid chromatography; LOD, limit of detection; MCL, maximum concentration level; MISPE, molecularly imprinted solid phase extraction; RSD, relative standard deviation; SALLE, salting-out assisted liquid–liquid extraction; TP, thiophanate; TPM, thiophanate-methyl; UV, ultraviolet.

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e.g. the synthesis of the solid sorbent or fiber and the need of special instrument. Furthermore, the process of SPE is relatively expensive and a problem about batch-to-batch reproducibility of the SPE column cartridges must be concerned. More importantly, it is very hard to extract benzimidazole fungicides efficiently from high salt matrices by using these extraction methods.

Fortunately, salting-out assisted liquid–liquid extraction (SALLE) provides a feasible alternative for high salinity sample preparation which is a technique based on LLE in which an appropriate concentration of salt is added to achieve the separation of aqueous phase from the partially miscible organic phase [10] and simultaneously the target solutes are extracted into the separated organic phase. Some of the organic solvents used in SALLE are acetonitrile, acetone, ethyl acetate and isopropanol and the salts commonly used are magnesium sulfate, ammonium sulfate, calcium chloride, potassium carbonate, and calcium sulfate [11]. This method coupled sample clean-up (e.g. acetonitrile deproteinization) with enrichment (via salting-out extraction) has been reported for water [10,11], biological [12–14], food [15,16], swine muscle [17], and drug [18] sample extraction processes. Also its prospective use for high salinity sample preparation is booming.

Herein, we propose the use of SALLE for extraction of four benzimidazole fungicides from three high salinity samples of seawater. Box–Behnken design and response surface were employed to assist finding optimum extraction conditions, quickly and reliably. To the best of our knowledge, this is the first demonstration for the optimization of SALLE by virtue of experimental design for benzimidazole fungicides analysis. The SALLE coupled with HPLC with the aid of experimental design was developed, validated and successfully applied for simultaneous separation and determination of the several benzimidazole fungicides in seawater samples.

2. Experimental

2.1. Chemicals and materials

Four benzimidazole fungicides standards of carbendazim (CBZ), fuberidazole (FBZ), thiophanate-methyl (TPM) and thiophanate (TP), derived from carbamic acid with chemical structure R–O–C(O)–N(CH₃)–R', where R is an alcohol, an oxime or a phenol, and R' is a hydrogen or a methyl group [1], were purchased from Sigma-Aldrich (Shanghai, China), and their chemical structures are shown in Fig. 1. HPLC-grade acetonitrile (ACN) was provided by J&K Chemical (Beijing, China). Dimethylsulfoxide (DMSO), NaCl, NaH₂PO₄, H₃PO₄, NaOH, and other affiliated chemicals were all obtained from

Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All solvents and chemicals were of analytical grade and used without further purification unless otherwise specified. HPLC-grade water was obtained by purifying demineralized water in a Milli-Q system (Millipore, Bedford, MA, USA), and was used throughout the work.

2.2. Apparatus and software

An HPLC instrument was provided by Skyray Instrument Inc. (Kunshan, Jiangsu, China), equipped with a UV detector. Separation was carried out on a Waters Arcus EP-C₁₈ column (150 mm × 4.6 mm id, 5 μm particle size). Analytes were eluted by a mixture of ACN and water (70/30, v/v) at a flow rate of 1 mL min⁻¹. Benzimidazole fungicides were monitored at 230 nm. All the samples were passed through microporous nylon filters of 0.45 μm pore sizes in diameter (Pall Corporation, USA).

Lingo software (LINDO Systems Inc., USA) was used to assist obtaining the optimum SALLE conditions by computing theoretical recovery. Matlab 7.5.0.342 (Mathworks Corporation, USA) was employed to develop the response surface. The script was run in Windows XP on a personal computer.

2.3. Preparation of standard and sample

Standard stock solutions containing 1000 μg mL⁻¹ of each benzimidazole fungicide were prepared by dissolving the required amounts of the standard in DMSO. They were stored in a refrigerator at 4 °C. Working solutions were prepared from the stock solutions by dilution with appropriate amounts of Milli-Q water.

Seawater was used as a model of high salt samples. They were collected from the coastal zone areas of Yantai City of China. Three surface water samples were from the junction of the Qinchui River and the Yellow sea (Seawater no. 1), the junction of the Xin'an River and the Yellow sea (Seawater no. 2), and Fisherman's Wharf of the Yellow sea (Seawater no. 3). The two junction water samples were taken near a sewage treatment plant of Yantai City. All the seawater samples were passed through microporous nylon filters with the pore sizes of 0.45 μm in diameter. The samples were kept under refrigeration at 4 °C in the dark. Several aliquots from 2 mL filtered water samples were spiked with the benzimidazole fungicide standard with different concentrations and followed by the SALLE procedure.

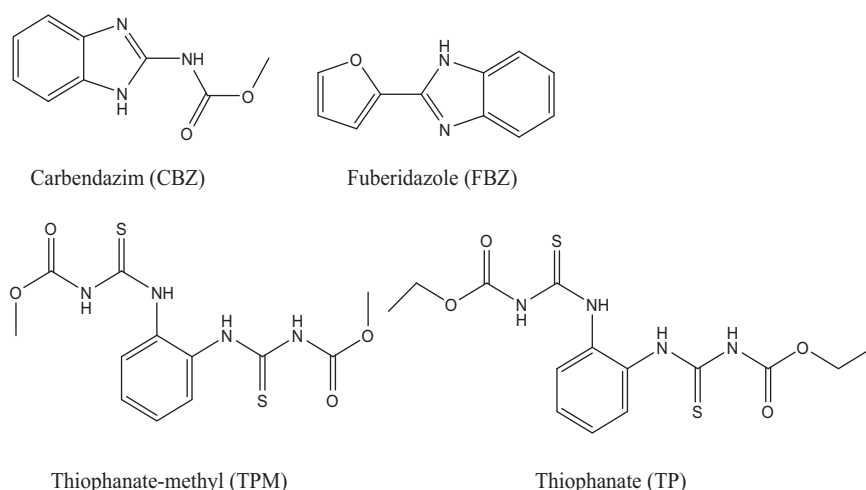


Fig. 1. Chemical structures of the benzimidazole fungicides analyzed.

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