

A Review of Sample Storage and Preservation of Polar Pesticides in Water Samples

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Key Words

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Solid-phase extraction
Freeze-drying

Summary

A review article with 35 references on the stability and preservation of samples of trace pesticides in water is presented. Stabilization and storage of samples are discussed together with methods of extraction and preconcentration.

Introduction

In the past much effort has been wasted on the analysis of a variety of samples of doubtful integrity and it has been frequently observed that valid analysis depends upon reliable sampling and storage.

Methods for collection and preservation are particularly important in the analysis of traces of pesticides in environmental samples. Maskareinec et. al. showed that acidification with HCl effectively prevented degradation of volatile compounds and allowed sample storage for 112 days [1]. The National Pesticide Survey (NPS) and the US EPA state that all monitored pesticides included in their programs should be stable in water for at least 14 days, after being inhibited biologically at pH < 3 and stored at 4 °C [2–6]. Organophosphorus (OP) pesticides have exhibited many stability problems and many of them have been eliminated from the NPS list (see Table I) because of this. The US EPA has withdrawn parathion-ethyl and methyl, azinphos-methyl, fenitrothion, demeton, fenthion and malathion from their list because of instability [7] although they are still included in European Community list. In a recent paper [8] it was reported that few organophosphorus compounds, some

of them common to the US EPA list, were stable at 4 °C in water from the river Axios in Greece at pH 8 over 8 days (see also Table I)

In some instances the degradation products of pesticides are more stable than the parent compounds so analysis should be aimed at the breakdown products [9, 11]. In general the half-lives of pesticides at low µg/L concentrations are, as one might expect, very much dependent on storage conditions (pH, exposure to light, and temperature). Biological degradation and adsorption on particulate matter are also important factors [9, 12]. For some compounds, degradation can be rapid; studies on the degradation of carbamate pesticides in water have shown that loss can take about 20 days for methiocarb sulfone, methiocarb sulfoxide and 3-ketocarbonylurea [13] whereas for carbaryl losses can approach 90 % in one day [10, 11]. In general, samples should be analyzed as soon as possible after collection.

In summary, losses of pesticides in water can be due mainly to hydrolysis, biodegradation, photolysis and evaporation. Each one of these mechanisms will depend upon the physicochemical properties of the pesticide and the water matrix. Volatilization from the water is also important, and this is related to the water solubility (WS) and vapor pressure (VP) of the pesticide. When this mechanism is predominant, storage in the original water matrix using tightly stoppered bottles in the dark at 4 °C might be the preferred method.

In this overview article various methods of sample storage and preservation are discussed. These include: (i) standard methods such as the addition of acids, freeze-drying, the use of SPE disks and cartridges and disposable SPE precolumns

Standard Methods of Storage

The main factors affecting the stability of analytes in water were discussed in a recent review article [14]. These factors include the character of the sample, the nature of the sample-container, and the conditions of storage (temperature, darkness, use of preservatives, time interval between sampling and analysis). A sum-