Measurement 60 (2015) 276–282

Contents lists available at ScienceDirect

Measurement

journal homepage: www.elsevier.com/locate/measurement

Development of a method for sampling and determination of corrosion inhibitors in modified atmospheres

Letícia Caetano da Silva [a], Elisabete Alves Pereira [b], Arnaldo Alves Cardoso [a,*]

[a] Universidade Estadual Paulista, Instituto de Química, Departamento de Química Analítica, P.O. Box 355, 14800-900 Araraquara, SP, Brazil
[b] Universidade Federal de São Carlos, Rodovia João Leme dos Santos, km 110, Bairro do Itinga, CEP 18052-780 Sorocaba, SP, Brazil

ARTICLE INFO

Article history:
Received 6 January 2014
Received in revised form 16 September 2014
Accepted 3 October 2014
Available online 28 October 2014

Keywords:
Volatile corrosion inhibitors (VCIs)
Amines
Protective atmosphere
Capillary electrophoresis
Suspended droplet

ABSTRACT

A simple and rapid analytical method was developed to determine concentrations of amines used as volatile corrosion inhibitors (VCIs) in protective atmospheres. A microdroplet (16.9 μL) of an absorbent solution (ethanol/water) was used to collect vapor phase VCIs. Simultaneous separation and determination of the amines was performed using capillary electrophoresis (CE), with indirect detection at a wavelength of 214 nm. The technique was used to measure monoethanolamine (MEA), monocyclohexylamine (MCHA), and dicyclohexylamine (DCHA). It was possible to detect amine in a standard atmosphere after a short time (10 min, including extraction and quantification), while best results were obtained for a total analysis time of 30 min. The method was used to analyze the composition of commercial materials used as VCIs, and revealed that DCHA was the main compound present, with the quantity of inhibitor contained in the plastic support being considerably greater than the amount in the vapor phase.

1. Introduction

Corrosion is a chemical phenomenon that occurs naturally due to the action of oxidizing substances on the surface of a material (usually metal), altering its properties and causing damage that can compromise its use [1]. Minimization of corrosion is therefore as important as the manufacture of the material. Metallic components and other metal artifacts are often transported and stored for long periods before they are actually used, during which corrosion can occur to the extent that the item becomes unusable, causing economic loss to the manufacturer. One way of minimizing the problem is to use temporary protective measures to prevent the degradation of metal items prior to their use [2].

The most common technique employed to provide temporary protection to metals, especially steel, is the use of volatile corrosion inhibitors (VCIs) [3–8], also known as vapor phase inhibitors (VPIs) [9]. These chemical compounds volatilize slowly, forming an atmosphere that acts to protect the metal surface [3–5].

Commercial corrosion inhibitors are composed of a mixture of organic and inorganic salts and polymeric compounds (nitrites, and salts of amines such as monoethanolamine, diethanolamine, and monocyclohexylamine, amongst others) [7,10,11], applied to the surface of a paper or plastic sheet that is used to wrap the metal items. This ensures that the atmosphere inside the wrapping contains the protective volatile species. The mechanism of inhibition depends on volatilization of the inhibitor, and subsequent condensation of the vapor onto the metal surface, where it reduces susceptibility to corrosion [5]. Due to their basic characteristics, certain amines such as monocyclohexylamine, diethylethanolamine, benzylamine, and morpholine can prevent corrosion by neutralization of acidic corrosive agents such as the carbon dioxide and sulfur dioxide gases [3]. The high volatility of monoethanolamine (MEA) and

---

* Corresponding author. Tel.: +55 16 3301 9736; fax: +55 16 3322 2308.
E-mail address: acardoso@iq.unesp.br (A.A. Cardoso).

http://dx.doi.org/10.1016/j.measurement.2014.10.005
0263-2241/© 2014 Elsevier Ltd. All rights reserved.

monocyclohexylamine (MCHA) (0.2 mm Hg and 10 mm Hg at 20 °C, respectively) [12] and the hydrophobic nature of dicyclohexylamine (DCHA) make these amines most suitable for use as corrosion inhibitors [3,13–15].

Despite the widespread use of VCIs as temporary protective agents, studies have revealed failures in the protection of metal parts during long periods of storage [2,6], which could be related to the quantity and type of chemicals used in the VCI formulation, or to the use of an inappropriate or date-expired material (treated paper or plastic). A difficulty in the quality control of VCIs is that direct assessment using corrosion testing often requires lengthy experimental procedures [13,15–17], while the thermogravimetric techniques frequently used to measure VCI volatility are unable to evaluate the quality of commercial products [14].

Although different models have been proposed to explain the mechanism of interaction of the VCIs with the surfaces of metals [5,13,18], it is recognized that effective protection depends on the equilibrium between the vapor and condensed phases. Volatilization and saturation of the atmosphere are therefore critical steps that govern the process, since phase equilibrium depends on the concentration of the vapor phase. There is therefore a fundamental need for methods that can determine the composition of atmospheres modified by the presence of volatile corrosion inhibitors, throughout the period of their use for the purpose of protection. Analysis of the composition of the vapor phase enables establishment of the minimum conditions necessary for effective use of the inhibitor, characterizing its useful lifetime and enabling comparisons to be made between products available on the market, as well as aiding the development of new formulations.

This work presents a simple and rapid technique for sampling and determination of the concentrations of VCIs in modified atmospheres. A solution containing MEA, MCHA, and DCHA was used as a source of vapor, and a suspended solution microdroplet was used to extract the amines present in the modified atmosphere. The extractant solution was subsequently analyzed using capillary electrophoresis (CE).

A microdroplet provides a surface for gas–liquid extraction, where the extractant solution is suspended and exposed to the test atmosphere, with gas phase analytes being solubilized at its surface. The analyte present in the vapor phase attempts to enter into equilibrium with the dissolved phase, hence transferring material from the atmosphere to the interior of the droplet. The dissolution of gases in liquids is governed by Henry's law, whereby the concentration of the dissolved component is proportional to the molar fraction of the gas phase component in the atmosphere above the liquid [19].

2. Experimental

2.1. Reagents and solutions

All the reagents used were analytical grade. 18-crown-6 ether, imidazole, and hydroxyisobutyric acid (HIBA) were obtained from Acros Organics (New Jersey, USA). The pH was adjusted using 1 mol L^{-1} hidrochloric acid and all solutions were prepared using deionized water (Milli-Q, Millipore, Bedford, MA, USA). Monoethanolamine (MEA) and monocyclohexylamine (MCHA) were obtained from Aldrich (Milwaukee, WI, USA), dicyclohexylamine (DCHA) and caprylic acid from Merck (Darmstadt, Germany), and acetone from Chemis (Joinville, SC, Brazil). Stock solutions were prepared using concentrations of 4.8×10^{-2} mol L^{-1} (MEA), 1.9×10^{-2} mol L^{-1} (MCHA), and 1.3×10^{-2} mol L^{-1} (DCHA). The ethanol/water (1:9 v/v) extractant solution used to produce the droplet was prepared daily using distilled ethanol (Merck).

2.2. System for generation of the suspended droplet

The system used to simulate the atmosphere obtained with the use of the VCIs consisted of a glass vessel with a volume of approximately 117 mL, fitted with a plastic screw cap. The microdroplet was produced using a glass syringe with a nominal volume of 1.00 mL (Fig. 1). A centrifuge tube (1.7 mL) from which the base had been removed was fitted to the center of the cap and acted as a septum, enabling the insertion of a syringe. After delivery of the source of amine vapor into the chamber, the system was sealed by closing the cap of the centrifuge tube. Throughout the period of the experiment, it was then possible to introduce a syringe containing the extractant solution into the chamber, in order to form a droplet directly exposed to the vapor. After sampling for a predetermined time, the solution droplet was withdrawn into the syringe and removed from the chamber, and the orifice was closed to maintain the internal vapor phase VCI concentrations practically unaltered.

2.3. Instrumentation

All the capillary electrophoresis experiments were performed using an Agilent model HP 3D CE instrument equipped with a high-voltage source (0–30 kV) operated at 18 kV, a diode array detector with a wavelength range of 190–600 nm, and a temperature controller. Sample injection was performed hydrodynamically (5 s, 30 mbar). The column used was a Polymicro Technologies (Phoenix, AZ, USA) fused silica capillary (75 µm i.d., 53 cm length

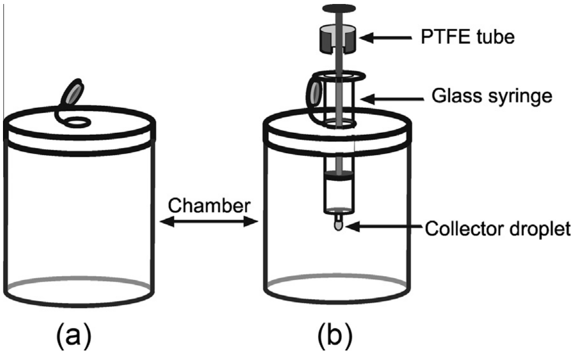

Fig. 1. Schematic diagram of the system used to generate VCI atmospheres: (a) glass chamber (volume = 117 mL) with opened cap of the adapted centrifuge tube and (b) system with the glass syringe in position with a suspended droplet to sample the VCI vapor.