Cathodic Stripping Determination of Water in Organic Solvents

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Abstract: A cathodic stripping voltammetry (CSV) method has been developed to determine water content in organic solvents based on electrooxidation of a gold electrode in the presence of water to form gold oxides upon anodic polarizations. Following cathodic potential scan, a sharp reductive stripping peak of gold oxides is generated and the magnitude of the peak current is related to the water content in the organic solvents. The method has been applied for determination of water in four commonly used water miscible organic solvents, acetonitrile, tetrahydrofuran, acetone and glacial acetic acid, with limits of detection of 60, 10, 40 and 10 ppm, respectively.

Keywords: Water determination · Cathodic stripping voltammetry · Organic solvent · Gold electrode · Karl-Fisher titration

1 Introduction

Water is one of the most common impurities in organic solvents. The presence of water in organic solvents can affect their basic physicochemical properties, such as viscosity, conductivity, density and electrochemical potential windows [1–3]. In synthetic chemistry, dehydration processes are often required to keep moisture from organic solvents when water-sensitive reagents are employed. In addition, acting as a by-product of many important reversible chemical reactions such as the Fischer esterification reaction, water content may influence the degree and rate of these chemical reactions [4,5]. Water also can affect the enzymatic activity in organic solvents which increased dramatically with the increase in water content [6]. However, water is ubiquitous and can easily adsorb on reaction vessel surfaces. Furthermore, adsorption from air is almost inevitable during storage or handling prior to use or during the course of an experiment conducted under benchtop laboratory. Therefore, an accurate in situ method for the determination of water content in organic solvents is highly desirable.

Currently, Karl Fischer titration (KF) is one of the most widely used method to determine traces of water in organic solvents and other non-aqueous solvents such as ionic liquids [7–13]. Though sensitive and easy to use, KF titration is an ex situ method, and suffers from errors associated with stability of the titrants and air tightness of the system [14,15]. Moreover, KF method is not reliable for determination of water in carboxylic acids, e.g. acetic acid, due to the esterification reaction that occurs with the primary alcohol (typically methanol) present in the titrants [16–18]. Other water determination methods including gravimetric IR and NMR spectroscopic techniques have also been applied for water determination in organic solvents [19–22]. However these techniques are time consuming, insensitive and require expensive instruments. Electrochemical method is an alternative choice due to its simplicity, low cost and fast response. Conductivity and impedance-based methods have been reported to determine trace water in organic solvents [23–25], which however are insensitive and require applying surface coatings to the electrodes and the addition of redox mediators to the solvent samples.

In this study, we report a novel electrochemical method for determination of water in organic solvents based on electrochemical formation and reduction of gold oxides in organic solvents with traces of water. The magnitude of the cathodic stripping peak current of gold oxides is proportional to the water content in the organic solvents. Recently, we have demonstrated the principle with satisfactory results for the determination of water in ionic liquids [26]. In this study, we extend the concept to organic solvents, which are currently widely used in chemistry and chemical industry.

2 Experimental

2.1 Reagents

AR grade acetonitrile (CH_3CN), tetrahydrofuran (C_4H_8O), acetone (CH_3COCH_3), glacial acetic acid (CH_3COOH) purchased from Sigma-Aldrich were purified and dried using solvent purification system (Pure Solv MD5, Innovative Technology, Inc.) prior to use. Analytical grade tetrabutylammonium perchlorate (98 %) was purchased from Sigma-Aldrich and used as supporting electrolytes.

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2.2 Apparatus and Procedure

Voltammetric measurements were carried out with an electrochemical workstation (CHI 660D, CH Instruments). The electrochemical cell for water determination in organic solvents contains three electrodes. The gold and platinum working electrodes were purchased from Cypress (Cypress System, Lawrence, KS). Prior to experiments, the working electrodes were polished with an aqueous 0.05 μm alumina slurry (CH Instrument, Texas, USA) on microcloth polishing pad (Buehler, Illinois, USA) and thoroughly rinsed with deionized water and acetone, then dried with low-lint tissue (Kimberly-Clark, Wisconsin, USA). Electrochemical cleaning was then carried out by cyclic voltammetry in 50 mM H_2SO_4 until reproducible characteristic voltammograms of Au and Pt electrodes were obtained. A platinum wire was used as a counter electrode and a silver wire sealed in a glass frit was used as the quasi-reference electrode (QRE). The potential of the Ag QRE was calibrated against an IUPAC recommended redox couple $Fc^{0/+}$ [27]. Karl Fischer titration measurements were performed with an 831 KF coulometer (Metrohm, Herisau, Switzerland).

The working solutions were prepared in a glove box by transferring the dried organic solvents into to a gas-tight electrochemical cell using a pipette, and then sealing the cell carefully with Blu-Tack to prevent water adsorption from air [28]. The voltammetric measurements were carried out outside the glove box. MillQ-water was then injected into the cell through a pre-opened hole, which is sealed when not injecting. The solution was mixed thoroughly by stirring for 1 min before the linear sweep voltammetric measurements taking place.

3 Results and Discussion

3.1 Formation of Gold Oxide in Organic Solvents in Presence of Water

It has been established that gold oxides are formed in aqueous solution on anodic scan via electroadsorbed layer of OH which undergoes a place exchange reaction with the metal to form a quasi 3D lattice of AuO [29,30].

$$Au + H_2O \leftrightarrow AuO + 2H^+ + 2e^- \qquad (1)$$
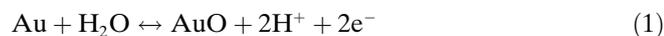
The growth of gold oxide is strongly related to the experimental conditions such as the surface structure of the gold electrode [31,32], the roughness factor [17], potential, electrolyte, and etc. In alkaline medium and high polarization potentials, a further oxidation from AuO to Au_2O_3 can occur [33].

$$2AuO + H_2O \leftrightarrow Au_2O_3 + 2H^+ + 2e^- \qquad (2)$$

On cathodic scan, the gold oxide film formed at positive potentials can be quickly (usually in a few seconds)

reduced back to elemental gold, regardless the thickness of the oxide films.

Similar voltammetric behaviors also have been observed in organic solvents containing water. Figure 1 shows the cyclic voltammograms obtained in 'dried' and 'wet' tetrahydrofuran at gold and platinum working electrodes, respectively. The cyclic voltammograms obtained in "dried" tetrahydrofuran show no significant Faradic processes in the potential range of −0.5 to 1.0 V vs. $Fc^{0/+}$ (Figure 1a). In contrast, with the addition of water content in tetrahydrofuran, both the gold oxide formation and reduction processes become evident and increase with water content. The voltammograms obtained at the Pt electrode exhibited analogous increase in reduction stripping peak current of platinum oxide with the increase of water concentration (Figure 1b). Nevertheless, due to the higher capacitance background current, the reductive peak of platinum oxide broadens and becomes less well-defined and not as sharp as that of gold electrodes.

The above results show that the voltammetry of gold and platinum electrodes in organic solvents is strongly
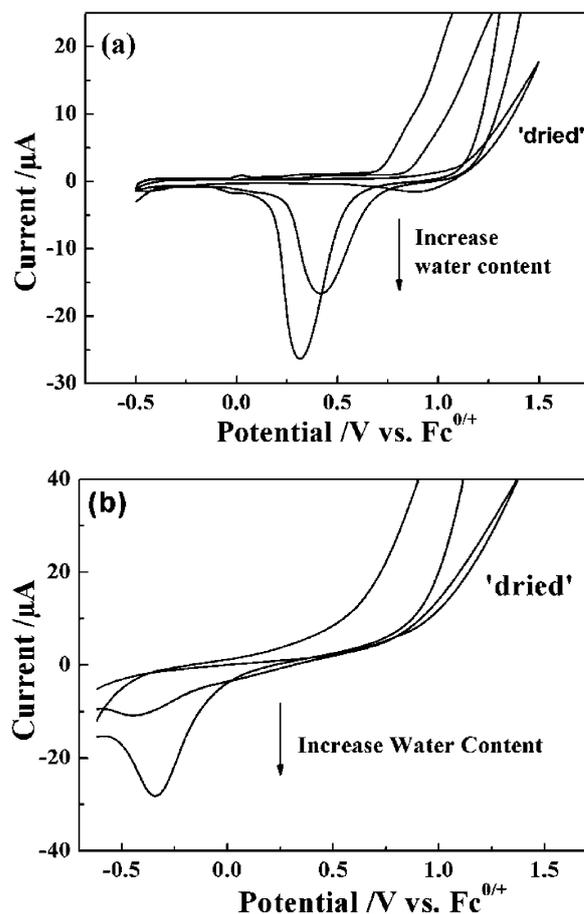

Fig. 1. (a) Cyclic voltammograms obtained at a gold electrode at the scan rate of 0.1 V s^{-1} in 'dried' tetrahydrofuran and after adding 1000 and 5000 ppm H_2O respectively. (b) Cyclic voltammograms obtained at a platinum electrode at the scan rate of 0.1 V s^{-1} in 'dried' tetrahydrofuran and after adding 5000 ppm H_2O.
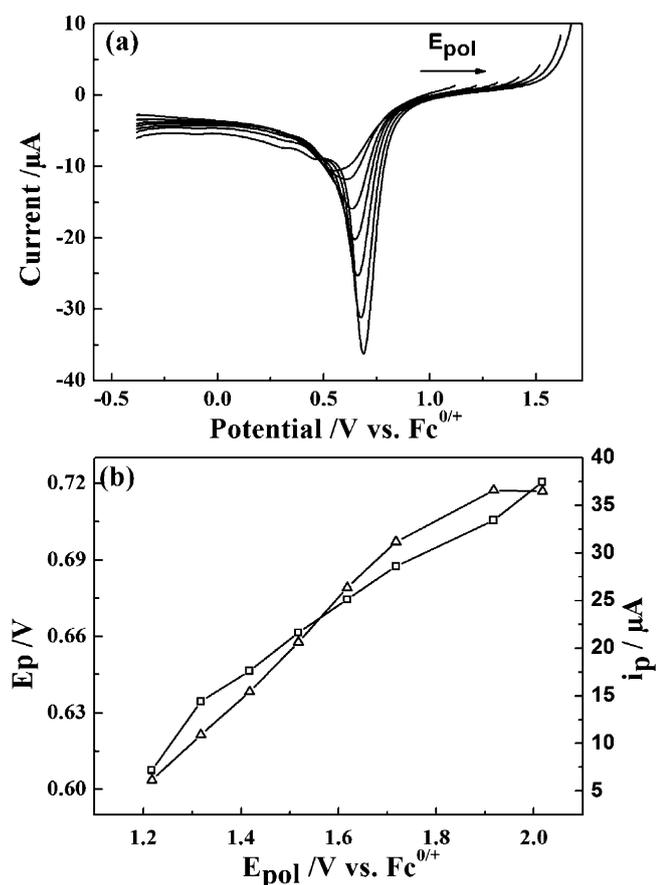
Fig. 2. (a) Linear sweep voltammograms obtained at a scan rate of $0.1\,V\,s^{-1}$ at gold electrode in acetonitrile with 1000 ppm H_2O after 45 s of polarization at varied potentials, E_{pol}. (b) Dependance of the stripping peak current, i_p (△) and peak potential, E_p (□) as a function of polarization potential, E_{pol}.

Fig. 3. (a) Linear sweep voltammograms obtained at a scan rate of $0.1\,V\,s^{-1}$ at a gold electrode in acetonitrile with 1000 ppm H_2O after polarizing the electrode at a potential of 1.9 V vs. $Fc^{+/0}$ for different time, t_{pol} (b) Stripping i_p (△) and E_p (□) as a function of polarization time t_{pol}.

water dependent. This phenomenon was utilized for determination of the water in organic solvents.

3.2 Dependence of Gold Oxides Reduction Process

The dependence of the oxidation of gold electrode on polarization potential (E_{pol}) and polarization time (t_{pol}) in organic solvents was further investigated. Figure 2a contains a series of linear sweep voltammograms obtained at a gold electrode at the scan rate of $0.1\,V\,s^{-1}$ in acetonitrile containing 1000 ppm H_2O as a function of the E_{pol} in the potential range from 1.2 to 2.0 V (vs. $Fc^{0/+}$). As shown in Figure 2b, the stripping peak current (i_p) increased from 5 µA to almost 36 µA when the peak potential (E_p) was shifted 0.11 V more positive and this is associated with the formation of thick gold oxide films. Thus, high E_{pol} can generate more gold oxides leading to higher stripping peak current.

The influence of polarization time (t_{pol}) was also investigated using gold electrode in acetonitrile containing 1000 ppm water by holding the potential at 1.9 V (vs. $Fc^{0/+}$) for different period of time ranging from 15 s to 50 s after which the potential was scanned to −0.3 V at
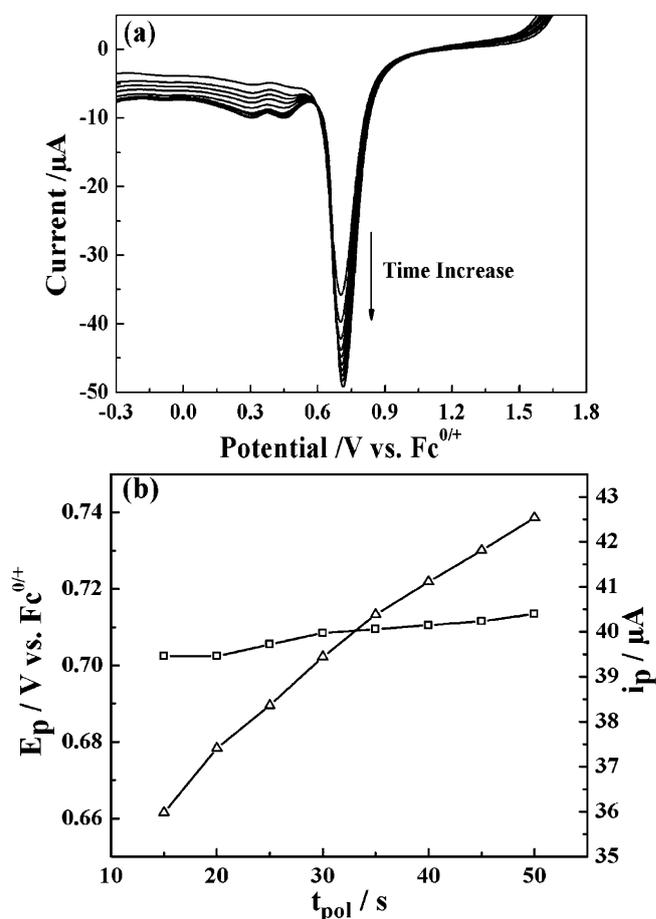
$0.1\,V\,s^{-1}$. The gold oxide stripping peak current increased gradually from 35 µA to approximately 43 µA as t_{pol} increases, while the peak potentials exhibited no significant change (Figure 3). It is therefore necessary to optimize the polarization potential and polarization time in order to improve the magnitude of the reduction stripping peak current.

3.3 Cathodic Stripping Voltammetric Determination of H_2O at a Gold Electrode

The above results suggest that the formation of gold oxide in organic solvents depends strongly on the polarization potential and polarization time. Moreover, due to different physicochemical properties of organic solvents such as potential window, hydrophobicity and viscosity, the characteristic voltammogram of gold differ in each solvent. Therefore the analytical protocol needed to be optimized for each solvent.

In this study, a cathodic linear sweep stripping voltammetry (CSV) was used to determine the water content for four commonly used organic solvents; acetonitrile, tetra-
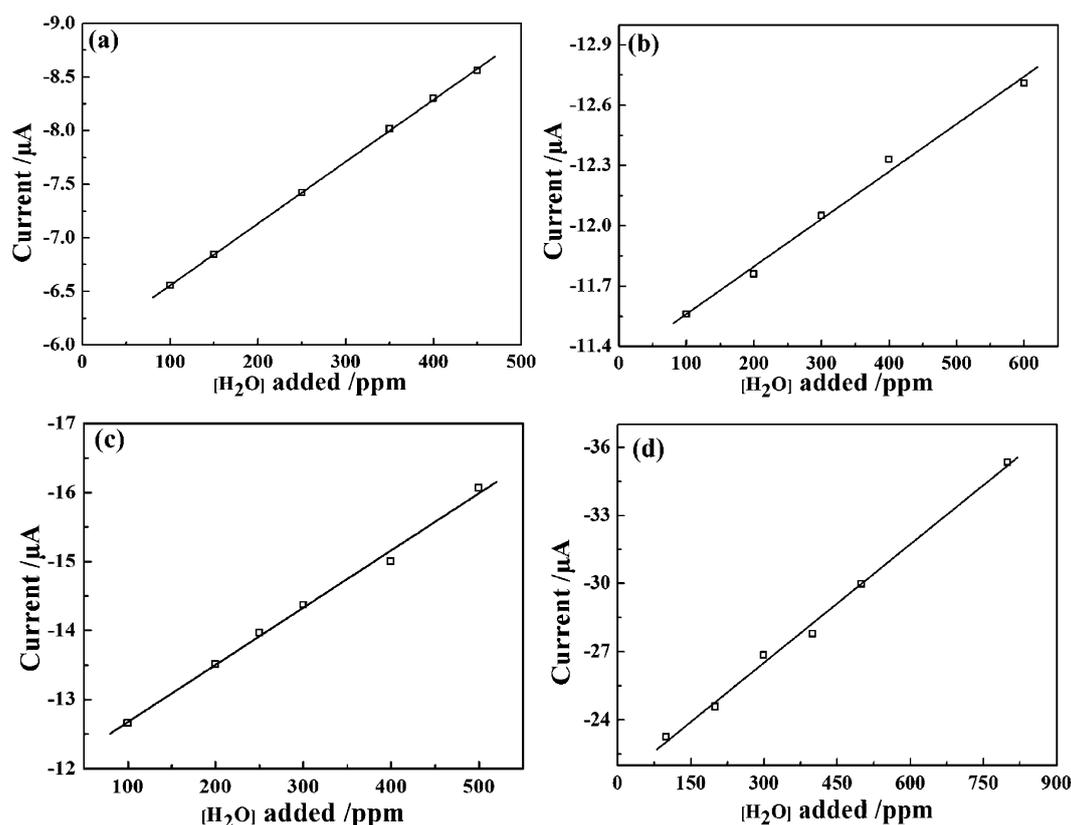
Fig. 4. (a) Dependence of cathodic stripping peak current on concentration of water added into (a) acetonitrile with polarization potential 1.9 V vs. $Fc^{+/0}$, polarization time 45 s, scan rate 0.1 V s^{-1}, (b) tetrahydrofuran with polarization potential 1.7 V vs. $Fc^{+/0}$, polarization time 45 s, scan rate 0.1 V s^{-1}, (c) glacial acetic acid with polarization potential 1.9 V vs. $Fc^{+/0}$ polarization time 45 s, scan rate 0.1 V s^{-1}, and (d) acetone with polarization potential 1.6 V vs. $Fc^{+/0}$, polarization time 45 s, scan rate 0.1 V s^{-1}.

hydrofuran, acetone and glacial acetic acid. Typically, a gold electrode was held at a positive potential (e.g. 1.9 V for acetonitrile, 1.7 V for tetrahdrofuran, 1.9 V for acetic acid and 1.6 V for acetone, respectively) for a period of time (e.g. 45 s) to accumulate gold oxides forming at the gold electrode surface and subsequently reduce the gold oxide by applying a linear cathodic potential sweep. The sharp cathodic stripping peak current increased gradually with the addition of water and was used to quantify the water content in the solvent. Finally, quantification of water content was performed by using the standard addition method.

Figure 4 shows the standard addition curves for four organic solvents, and their analytical characteristics are summarized in Table 1. Using the definition of 3 and 10

times the signal-to-noise ratio as limit of detection (*LOD*) and limit of quantification (*LOQ*) respectively [34], the *LOD* and *LOQ* data for the four solvents are also given. Table 1 shows that low *LOQs* and *LODs* are obtained with the gold electrode method, which is attributed to sharp stripping peak and the very low background noise for this surface-confined process.

Furthermore, the method was applied for determination of water in very "wet" organic solvents. For very 'wet' samples, the KF method becomes unsuitable due to prolonged titration time and excessive reagent consumption. Table 2 sums up the dependence of cathodic stripping peak current on water content in very 'wet' organic solvents. For acetonitrile, tetrahydrofuran and acetone, the first linear range is always more sensitive (higher

Table 1. Linear ranges, calibration equation, limit of quantification (*LOQ*) and limit of detection (*LOD*) of cathodic stripping voltammetry method for the determination of water in acetonitrile, tetrahydrofuran, glacial acetic acid and acetone. The linear sweep conditions are as in Figure 4.

Organic solvent	Linear range (ppm)	Calibration equation	R^2	*LOQ* (ppm)	*LOD* (ppm)
Acetonitrile	176–526	i_p (A) $= -5.98 \times 10^{-6}$ (A) -5.77×10^{-9} A/ppm ([H$_2$O]/ppm)	0.9997	200	60
Tetrahydrofuran	165–665	i_p (A) $= -11.33 \times 10^{-6}$ (A) -2.31×10^{-9} A/ppm ([H$_2$O]/ppm)	0.9965	35	10
Glacial acetic acid	100–500	i_p (A) $= -11.85 \times 10^{-6}$ (A) -8.28×10^{-9} A/ppm ([H$_2$O]/ppm)	0.9935	135	40
Acetone	100–800	i_p (A) $= -21.30 \times 10^{-6}$ (A) -1.70×10^{-8} A/ppm ([H$_2$O]/ppm)	0.9943	35	10

Table 2. Linear ranges and calibration equation of cathodic stripping voltammetry method for the determination of water in 'wet' acetonitrile, tetrahydrofuran, glacial acetic acid and acetone. The linear sweep conditions are as in Figure 4.

Organic solvent	Linear range (ppm)	Calibration equation	R^2
Acetonitrile	1×10^3–1×10^4	i_p (A) $= -8.38 \times 10^{-6}$ (A) -1.210×10^{-9} A/ppm ($[H_2O]$/ppm)	0.9940
	1×10^4–6×10^4	i_p (A) $= -19.99 \times 10^{-6}$ (A) -1.524×10^{-10} A/ppm ($[H_2O]$/ppm)	0.9904
Tetrahydrofuran	1×10^3–4×10^3	i_p (A) $= -6.06 \times 10^{-6}$ (A) -1.597×10^{-9} A/ppm ($[H_2O]$/ppm)	0.9959
	2×10^4–7×10^4	i_p (A) $= -11.73 \times 10^{-6}$ (A) -1.917×10^{-10} A/ppm ($[H_2O]$/ppm)	0.9968
Glacial acetic acid	2×10^3–7×10^3	i_p (A) $= -15.67 \times 10^{-6}$ (A) -2.386×10^{-10} A/ppm ($[H_2O]$/ppm)	0.9912
	1×10^3–6×10^4	i_p (A) $= -12.63 \times 10^{-6}$ (A) -3.877×10^{-10} A/ppm ($[H_2O]$/ppm)	0.9906
Acetone	1×10^3–8×10^3	i_p (A) $= -31.70 \times 10^{-6}$ (A) -1.660×10^{-9} A/ppm ($[H_2O]$/ppm)	0.9969
	2×10^4–7×10^4	i_p (A) $= -36.14 \times 10^{-6}$ (A) -3.995×10^{-10} A/ppm ($[H_2O]$/ppm)	0.9948

Table 3. Determination of water in organic solvent samples by KF method and the proposed CSV method, and recovery analysis using the CSV method.

Sample	Karl Fischer (ppm)	CSV Method (ppm)	Added (ppm)	Found (ppm)	Recovery (%)
Tetrahydrofuran	670	628	250	255	102.1
Acetonitrile	577	593	250	241	96.4
Acetone	6667	6585	5000	5164	95.2
Acetic Acid	[a]	5144	10000	10961	109.1

[a] Could not be determined due to the esterification side reactions.

slope) than the second ones. This could be attributed to the fact that at very high water content, the electrode surface area becomes the limiting factor for gold oxides formation, and larger surface area electrode will be required. Interestingly, for the glacial acetic acid, the second linear range is more sensitive, which might be caused by more free hydrogen ions becoming available in the media which increases the conductivity of solvents dramatically [35,36].

To validate the accuracy and reliability of the proposed method for practical application, the water content in 4 organic solvent samples were determined and compared with Karl Fisher titration (Table 3). The samples were prepared by exposing "dried solvents to air on bench for 30 min. Each measurement was carried out thrice and the average value summarized in Table 3. The results show CSV method is in reasonable accordance with the KF method. Furthermore, the sample solvents were spiked with water and the recovery determined by using the CSV method. Good recovery results ranging from 95.2 % to 109.1 % are obtained, indicating the proposed CSV method is rather reliable in determining water content in both dry and very wet organic solvents.

4 Conclusions

A simple electrochemical method has been developed to determine water content in organic solvents. Based on the voltammetry of gold electrodes in the presence of water, a cathodic stripping voltammetric method has been established for four common organic solvents. The method provides a useful alternative to conventional Karl Fischer titration, and offer significant advantages such as i) detection of water in carboxylic acids without suffering from esterification side reaction, ii) in situ detection,

which can minimize the errors such as water adsorption from air associated with ex situ detection, iii) suitable for very wet samples, iv) reagentless. Furthermore, its electrochemical nature makes it suitable for water detection in small sample volume as well as for making miniaturized and /or disposable water sensor.

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