

Detection of Food Additives by Voltammetry at the Liquid–Liquid Interface

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Electrochemistry at the liquid–liquid interface enables the detection of nonredoxactive species with electroanalytical techniques. In this work, the electrochemical behavior of two food additives, aspartame and acesulfame K, was investigated. Both ions were found to undergo ion-transfer voltammetry at the liquid–liquid interface. Differential pulse voltammetry was used for the preparation of calibration curves over the concentration range of 30–350 μM with a detection limit of 30 μM . The standard addition method was applied to the determination of their concentrations in food and beverage samples such as sweeteners and sugar-free beverages. Selective electrochemically modulated liquid–liquid extraction of these species in both laboratory solutions and in beverage samples was also demonstrated. These results indicate the suitability of liquid–liquid electrochemistry as an analytical approach in food analysis.

KEYWORDS: Voltammetry; liquid–liquid interface; aspartame; acesulfame K; artificial sweetener

INTRODUCTION

Electrochemistry at the interface between two immiscible electrolyte solutions (ITIES) offers several advantages in the areas of electroanalysis and sample preparation. It is based on the transfer of ions across the liquid–liquid interface induced by the application of a potential difference between the two phases. Any charged chemical species is susceptible to transfer across the interface if the energy provided is sufficient. This makes electrochemistry at the ITIES a very attractive analytical technique for the detection of nonredoxactive species. Electroanalysis at the ITIES was successfully applied to numerous analytes, such as Ag^+ ions (1), dopamine (2–4), Cr(VI) (5), amino acids (6), peptides (7, 8), proteins (9), carbohydrates (10–12), dendrimers (13), and drugs (14). Electrochemistry at the ITIES can also be used as a sample preparation technique as potential-controlled selective extraction of ions is possible (15, 16) so that ions of interest in a mixture can be extracted by tuning the applied potential difference between the two liquid phases or between an aqueous liquid phase and an organic gel phase. Selective extraction of ions from a mixture as well as coextraction is possible, offering wide possibilities in sample preparation and cleanup (15). Unfortunately, the analytical performance characteristics have prevented electrochemistry at the ITIES from finding wide applications in the analysis of real samples and materials. One way to improve the analytical performance is to use microscopic liquid–liquid interfaces, which enhance the mass transport of analyte species (linear to radial diffusion) and provide better limits of detection (17).

Electrochemical methods have been widely applied to the determination of contaminants in foods. Stripping voltammetry techniques were used for the determination of heavy metals in beverages (18–21). Electroanalysis and biosensor technologies were successfully employed for the detection of sulfites in food samples (22, 23). Amino acids and proteins can also be determined in food samples by electroanalysis (24). Electrochemical detectors were implemented in sequential injection analysis (25) and chromatographic systems for analysis of food samples (26).

This paper presents the application of liquid–liquid electrochemistry for the detection and extraction of analytes in real food samples. We have selected aspartame and acesulfame K (Figure 1) as two model food additives to demonstrate the

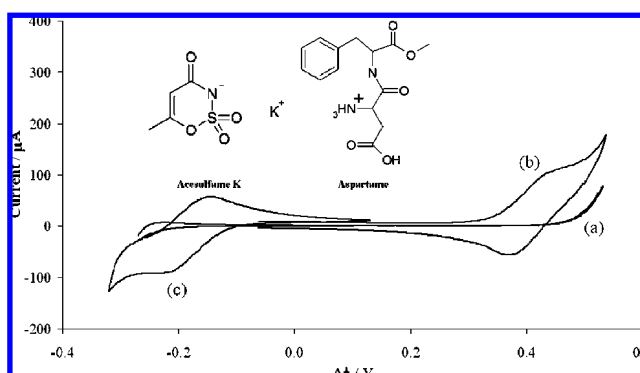


Figure 1. CV in the absence (a), in the presence of 2.1 mM of aspartame (b), and in the presence of 1.9 mM of acesulfame K (c). $\nu = 5 \text{ mV s}^{-1}$; electrochemical cell 1. Inset: Chemical structures of aspartame and acesulfame K at pH 2.

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suitability of electrochemistry at the ITIES as a sensitive electroanalytical strategy and as an efficient extraction method in food sample analysis. Aspartame and acesulfame K are synthetic sweeteners that are very frequently used in sugar-free foods and beverages. Aspartame is the methyl ester derivative of an aspartyl-phenylalanine dipeptide. It possesses a carboxylic group and an amine group and at pH 2 is fully protonated with a charge of +1. It is ca. 180 times sweeter than sucrose but with a very low energetic contribution, which makes it a very popular sugar substitute in sugar-free diets. It is present in numerous food articles available in the marketplace. Acesulfame K is a sweetening, noncaloric potassium salt used in conjunction with aspartame. Various methods of detection have been used for the determination of their levels in food samples. Liquid chromatography is one of the methods of choice in conjunction with various detection systems: amperometric (27), coulometric (28), mass spectrometry (29), spectrofluorometry (30), light scattering (31), and conductivity (32). Other separation techniques have also been used, such as capillary electrophoresis (33, 34), gas chromatography (35), and capillary isotachopheresis (36). Flow injection systems with spectrophotometric determination were also designed (37, 38). Aspartame levels were determined in food samples using enzymatic biosensors (39–41). Furthermore, Fourier transform infrared spectroscopy proved to be useful for acesulfame K and aspartame (42). The majority of these methods are based on bulky instrumentation, which can be applied in central laboratories. Simpler methods based on electrochemical properties of the compounds offer significant opportunity for low-cost and routine analysis.

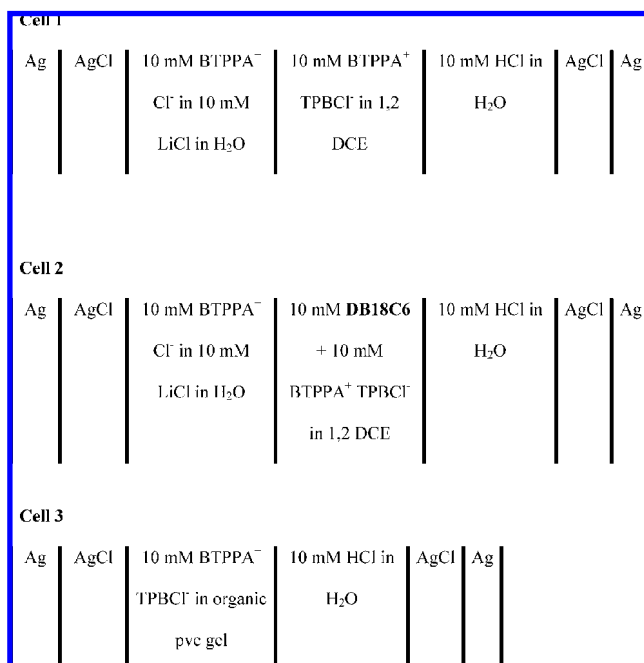
We present here the electrochemistry of aspartame and acesulfame K at the ITIES. The electrochemical characteristics for both nonfacilitated and facilitated transfers are presented as well as the electroanalytical performance of their behavior at of the ITIES. Food samples were analyzed to test the performance of this analytical method. Finally, electrochemically modulated extraction of the two ions was investigated, as the basis of a possible sample preparation/extraction methodology.

MATERIALS AND METHODS

Reagents. The two analytes, aspartame [*N*-(*L*- α -aspartyl)-*L*-phenylalanine methyl ester] and acesulfame K [6-methyl-1,2,3-oxathiazin-4(3*H*)-one 2,2-dioxide potassium salt], were purchased, together with all other chemicals, from Sigma-Aldrich Ireland Ltd. and used without further purification. Stock solutions of aspartame and acesulfame K were prepared on a daily basis in the aqueous electrolyte solution 10 mM HCl. The organic electrolyte salt was prepared by metathesis of bis-(triphenylphosphoranylidene) ammonium chloride (BTTPPA⁺ Cl⁻) and potassium tetrakis(4-chlorophenyl)borate (K⁺ TPBCl⁻) to obtain BTTPPATPBCl following the well-known experimental procedure (43). The organic electrolyte solution was prepared in 1,2-dichloroethane (1,2-DCE).

Voltammetry Experiments. All voltammetry experiments were performed with an Autolab PGSTAT30 potentiostat (Ecochemie, The Netherlands). A customized glass liquid–liquid electrochemical cell from AGB (Dublin, Ireland) was used for the liquid–liquid voltammetry experiments. The interfacial potential difference was controlled using two Ag|AgCl wires (one in each phase), and the current was measured using two Pt mesh counter electrodes (one in each phase). The silver wires were coated with silver chloride by immersion in a concentrated solution of FeCl₃. The geometric area of the interface was 0.785 cm² and was flat in appearance. In the experiments presented here, a positive current corresponds to the transfer of a cation from the aqueous phase to the organic phase or of an anion from the organic phase to the aqueous phase. A negative current is the result of the transfer of a cation from the organic phase to the aqueous phase or of an anion from the aqueous phase to the organic phase. Cyclic voltammetry (CV) was used for the investigation of the electrochemical behavior of both aspartame

Scheme 1



and acesulfame K. The scan rate used was 5 mV s⁻¹. Calibration curves of both food additives were constructed by differential pulse voltammetry (DPV). The DPV waveform parameters were as follows: modulation amplitude, 30 mV; modulation time, 75 ms; and increment, 2 mV. All experiments were done in triplicate. **Scheme 1** describes the three electrochemical cells used for the experiments presented here.

Analytical Samples. The samples selected for these studies were a tabletop sweetener, two sugar-free colas, three sugar-free lemonades, and a sugar-free apple juice, all obtained locally. All of these samples contained both acesulfame K and aspartame. Their levels were determined using DPV with the waveform parameters as described above for the calibration curves. The method of standard additions was used to determine the aspartame and acesulfame K levels. Four additions of a known concentration of the target analyte were made. For the analysis of the tabletop sweetener, the whole content of a sachet was dissolved in 20 mL of 10 mM HCl. An aliquot (300 μ L) of this solution was then added to the aqueous phase of the electrochemical cell. The beverages were added directly to the aqueous phase of electrochemical cell 1. Stock solutions at 1 mM concentrations of the two analytes in 10 mM HCl were made. Additions of 50 μ L to the electrochemical cell were made to build the different calibration curves. The initial volume of the electrochemical cell was 1.5 mL. The 95% confidence limits for the content of the target analytes in the samples were calculated according to the method described by Miller and Miller (44). The analytical results from the electrochemical method were compared to data from a standard liquid chromatographic method as run by the Public Analyst's Laboratory in Cork.

Electrochemically Modulated Extraction. An in-house-constructed liquid–liquid extraction cell (15, 16) was used for the extraction experiments. The organic phase was gellified using polyvinyl chloride (PVC) and placed in a cavity with the aqueous phase flowing above it. Ag|AgCl reference and Pt counter electrodes were placed in each phase for these experiments. The organic phase gel was prepared as follows: BTTPPATPBCl was dissolved in 1,2-DCE, and the solution was stirred at 80 °C for 5 min. Low molecular weight PVC was added to a concentration of 10% w/v, and the temperature was held for an additional 5 min. The solution temperature was then raised to 100 (5 min) and 120 °C (10 min), plus a few more minutes at a temperature no higher than 150 °C. The gel was then placed in the cavity in the electrochemical extraction cell. The electrochemical extraction cell was connected to a flow system (syringe pump and six-port valve with a 100 μ L injection loop). The flow rate of the aqueous phase was 1 mL min⁻¹. Extraction experiments were performed at constant potential,

Table 1. Electrochemical Characteristics of Aspartame and Acesulfame K^a

analyte	$\Delta\phi_{1/2}$ (V)	$\delta\Delta\Phi$ (V)	$\Delta\phi_{1/2,f}$ (V)	$\ln \beta$
aspartame	0.402	0.080	0.186	9.2
acesulfame K	-0.142 ^b	0.095	0.080 ^c	10.1 ^d

^a $\Delta\phi_{1/2}$ is the half-wave potential for simple ion transfer, the average of the forward and reverse transfer potentials. $\delta\Delta\Phi$ is the difference between the forward and the reverse transfer potentials. $\Delta\phi_{1/2,f}$ is the half-wave potential for facilitated ion transfer, the average of the forward and reverse transfer potentials. ^b Value for acesulfame anion transfer. ^c Value for K⁺ facilitated transfer. ^d From ref (4).

with the current monitored as a function of time. After stabilization of the background current, the sample solution studied was injected. These experiments were performed with a CHI 660B potentiostat (CH Instruments, Texas).

RESULTS AND DISCUSSION

Simple Ion Transfer. Aspartame and acesulfame K were characterized electrochemically by CV (Figure 1). Both analytes were seen to undergo simple ion transfer across the ITIES. The electrochemical parameters determined are summarized in Table 1. A well-defined pair of peaks was observed for both food additives. The nonfacilitated transfer of aspartame occurred at +0.402 V. The difference between the forward and the reverse peak potentials was ca. 0.080 V, which is close to the theoretical value of $0.059/z$ V, where z is the charge of aspartame. At the pH studied (pH 2), $z_{\text{aspartame}}$ is equal to +1 as both the amine and the carboxylic groups are protonated. The value obtained indicates that the transfer of aspartame across the interface is a reversible process. The acesulfame K electrochemical behavior was investigated in a similar manner. Its transfer potential was measured at -0.142 V, with a difference between forward and reverse peak potentials at ca. 0.095 V. For both analytes, the peak current varied linearly with the square root of the scan rate, indicating that their transfer is a diffusion-controlled process (not shown).

Facilitated Ion Transfer. The facilitated transfer of the target analytes was also investigated, as this offers the opportunity to shift the transfer potential to more suitable locations within the available potential window. Dibenzo-18-crown-6-ether (DB18C6) is a widely used ionophore for facilitated ion transfer of cations, especially K⁺, Na⁺, and NH₄⁺. It has been extensively used for the transfer across the ITIES of ions such as K⁺ (45), dopamine (2, 3), amino acids (6), and peptides (7, 8), whereby DB18C6 dissolved in the organic phase facilitates the transfer of cations by forming a complex at the liquid-liquid interface. It was found that the addition of DB18C6 to the organic phase facilitated the transfer of aspartame by complexation via its amine group, the same complexation mechanism as for dopamine and peptides. The transfer potential of aspartame in the presence of DB18C6 was lowered to +0.186 V. The addition of 50 μM acesulfame K to a 200 μM aspartame solution resulted in a single peak of higher intensity than for aspartame on its own (Figure 2). This increase was due to the facilitated transfer of K⁺. The inability to distinguish the transfer of K⁺ from the transfer of aspartame therefore prevents the use of DB18C6-facilitated ion transfer voltammetric determination of aspartame levels when acesulfame K or any other source of K⁺ is present. The association constant, β , between aspartame and DB18C6 was measured according to the protocol previously used to calculate β between calixarene and K⁺ (46). To determine β , aspartame was employed in molar excess as compared to DB18C6. The facilitated transfer of aspartame was studied in these conditions, and the transfer potential, $\Delta\phi^{1/2}$, was measured

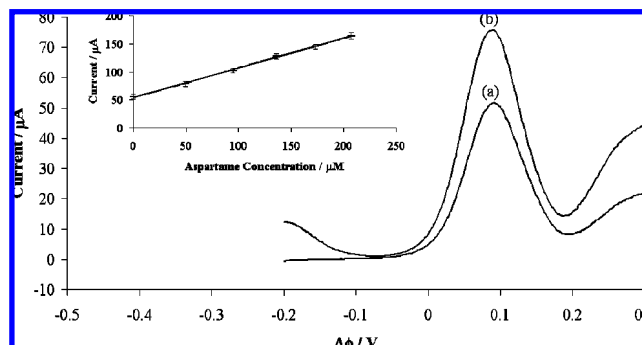


Figure 2. Background-subtracted differential pulse voltammograms of the facilitated transfer of 200 μM aspartame in the absence (a) and in the presence of 50 μM acesulfame K. DPV parameters were as follows: amplitude, 30 mV; modulation time, 75 ms; and increment, 2 mV. Electrochemical cell 2. Inset: peak current values for aspartame with increasing concentration of acesulfame K. Electrochemical cell 2.

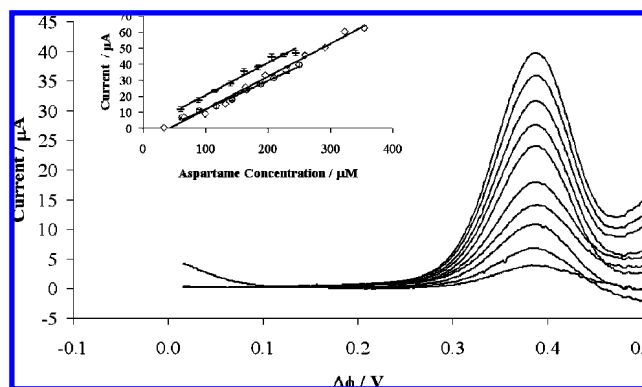


Figure 3. Background-subtracted differential pulse voltammograms of the transfer of aspartame in the absence of both acesulfame K and DB18C6. Increasing concentration of aspartame (bottom to top): 33, 62, 91, 118, 143, 167, 189, 210, 231, and 250 μM . DPV parameters were as follows: amplitude, 30 mV; modulation time, 75 ms; and increment, 2 mV. Electrochemical cell 1. Inset: calibration curves for aspartame in the absence (○) of both acesulfame K and DB18C6 (calibration range, 62–250 μM) in the presence (—) of acesulfame K (calibration range, 61–244 μM) and in the presence of DB18C6 (◇) (calibration range, 33–354 μM).

for increasing concentrations of aspartame. The value for β is given by the following equation:

$$\ln \beta = \frac{zF}{RT} (\Delta\phi^0 - a) \quad (1)$$

where z is the charge of the transferred ion, F is the Faraday constant, R is the molar gas constant, T is the temperature in Kelvin, $\Delta\phi^0$ is the nonfacilitated transfer potential of aspartame, and a is the intercept of the plot $\Delta\phi^{1/2}$ vs \log [aspartame]. The value obtained in this way for $\ln \beta$ was 9.2, which is slightly lower than the value obtained for K⁺ at the ITIES (4). This indicates a higher stability of the complex formed between K⁺ and DB18C6 than between aspartame and DB18C6, confirming that DB18C6 in the organic phase will not differentiate between the two ions.

Analytical Characteristics. DPV was selected as the electroanalytical technique to achieve low levels of detection. Background-subtracted DPVs for aspartame concentrations ranging from 32 up to 354 μM are shown in Figure 3. A sensitivity of $0.180 \pm 0.014 \mu\text{A} \mu\text{M}^{-1}$ ($R = 0.996$; $N = 9$) was obtained. The sensitivity for aspartame in the presence of acesulfame K was $0.204 \pm 0.024 \mu\text{A} \mu\text{M}^{-1}$ ($R = 0.992$; $N =$

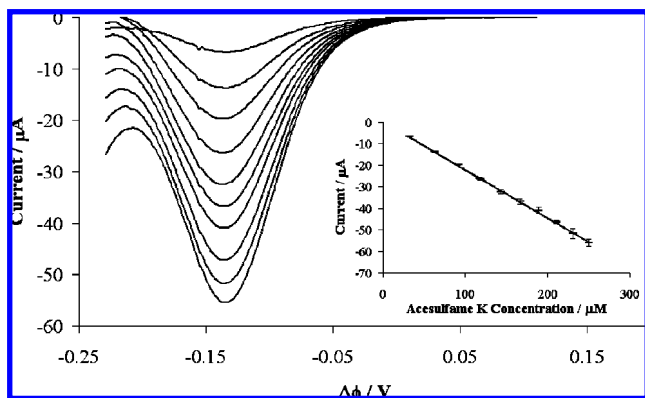


Figure 4. Background-subtracted differential pulse voltammograms of the transfer of acesulfame K. Increasing concentration (bottom to top): 33, 62, 91, 118, 143, 167, 189, 211, 231, and 250 μM . Experimental parameters are as in **Figure 3**. Inset: calibration curve for acesulfame K.

9), which is slightly higher than the sensitivity for the aspartame on its own but within the range of the standard deviation. These experiments show that the presence of acesulfame K in the solution did not interfere with the signal of the nonfacilitated transfer of aspartame. A calibration curve for the facilitated transfer of aspartame was also prepared. The sensitivity measured was $0.2042 \pm 0.014 \mu\text{A} \mu\text{M}^{-1}$ ($R = 0.997$; $N = 11$). The presence of DB18C6 did not increase the sensitivity for aspartame detection, as expected, since the ion transfer reaction is controlled by diffusion of the analyte in the aqueous phase regardless of whether it undergoes a facilitated or simple ion transfer. However, the lowest concentration measured for the nonfacilitated transfer of aspartame was $60 \mu\text{M}$, but the presence of DB18C6 allowed the detection of $30 \mu\text{M}$ aspartame. A calibration curve of acesulfame K was also constructed between 33 and $250 \mu\text{M}$ by DPV (**Figure 4**). The sensitivity measured was $-0.2238 \pm 0.0080 \mu\text{A} \mu\text{M}^{-1}$ ($R = 0.999$, $N = 10$). The sensitivities for both acesulfame K and aspartame are of the same order of magnitude, as could be expected, since they have the same absolute charge and have similar molecular masses. The limits of detection achieved may be easily lowered by various strategies, such as use of miniaturized ITIES and of differential pulse stripping voltammetry. However, the limits of detection achieved in this study proved to be sufficient for the applications described in the following section.

Food and Beverage Sample Studies. The concentrations of aspartame and of acesulfame K were determined in three types of food samples to test the performance and practicality of electroanalysis at the ITIES as a method for food analysis. The three samples were a tabletop sweetener, five sugar-free soda drinks, and an apple juice without added sugar. The method of standard additions was used to determine the concentration of the food additives studied in these seven samples (**Figure 5**). Unfacilitated transfers of aspartame were employed so as not to have interference from K^+ . Additions of known concentrations of the analyte resulted in an increase of the peak current measured. The plot of current vs analyte concentration added was linear and allowed the determination of the concentration of the analyte in the samples studied. **Table 2** presents the concentrations obtained. For the cola, the weight concentration of aspartame is 10 times greater than that of acesulfame K. For a tabletop sweetener sachet, the aspartame and acesulfame K values were within the range of the values reported in the literature for tabletop sweeteners studied by various analytical methods. For acesulfame K in cola and for both aspartame and

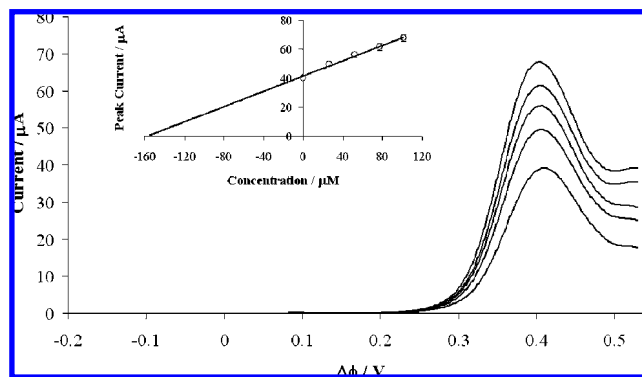


Figure 5. Determination of aspartame in sugar-free cola by standard additions method. Background-subtracted differential pulse voltammograms of the transfer of aspartame. Experimental parameters are as in **Figure 3**. Inset: transfer peak current vs concentration added plot. Cell 1.

acesulfame K in fruit juice, our values differ greatly from the literature values. However, this comparison does not have much significance as there is only one value in the literature. The concentrations calculated from the standard additions experiments are reported in **Table 2** and are compared to the values obtained by a standard analytical method. It can be seen that reasonable agreement between the two analytical methods was found for the concentrations of acesulfame K. However, the aspartame concentrations obtained by the electrochemical method were much higher than the ones given by the standard method. For the sugar-free colas and lemonades, the standard addition graph slope values are similar to the ones obtained for the calibration curves of acesulfame K in pure solution. This indicates that no other species are contributing to the transfer currents attributed to the analytes in this matrix. However, for aspartame, the slope is much lower than that obtained for the calibration curve, indicating a matrix effect due to the different compounds present in the sample, which lowers the sensitivity. As a result, the concentrations obtained for aspartame are inaccurate. This may be due to the presence of an interfering compound (or compounds) in the sample matrix, which contributes to the current measured for aspartame. This issue requires further investigation, although it can be stated at present that the interference is not potassium, as DB18C6 was not present in the organic phase, and thus, potassium cannot be transferred across the ITIES.

Electrochemically Modulated Extraction. Aspartame and acesulfame K in background electrolyte of aqueous 10 mM HCl solutions and from real samples were extracted by a potentiostatic liquid–liquid extraction method (15, 16). The extraction of these two analytes was investigated as a function of the applied interfacial potential difference. Using the transfer currents measured, hydrodynamic voltammograms (HDVs) were built (**Figure 6**). Below $\Delta\phi = -0.250 \text{ V}$, the potential difference was sufficiently negative to extract acesulfame K from the flowing aqueous solution. At a potential difference greater than $\Delta\phi = +0.25 \text{ V}$, aspartame was extracted from the flowing aqueous solution. There was no coextraction of the two ions studied between $\Delta\phi = -0.25$ and $\Delta\phi = +0.25 \text{ V}$. The charge transferred for aspartame during the extraction at $\Delta\phi = +0.376 \text{ V}$ was $107.6 \pm 5.8 \mu\text{C}$. For acesulfame K, a charge of $-99.0 \pm 6.3 \mu\text{C}$ at an extraction potential of $\Delta\phi = -0.349 \text{ V}$ was obtained. If we consider that $100 \mu\text{L}$ of a 1 mM aspartame or acesulfame K solution in 10 mM HCl was injected, according to Faraday's law, a maximum charge of 9.65 mC can be expected if 100% extraction efficiency was obtained. As a result, 1% of the aspartame or acesulfame K injected was extracted.

Table 2. Concentrations of Aspartame and Acesulfame K Determined in Samples^a

sample		aspartame	acesulfame K
tabletop sweetener	volume added	300 μL	50 μL
	slope	0.1430 $\mu\text{A } \mu\text{M}^{-1}$	-0.1162 $\mu\text{A } \mu\text{M}^{-1}$
	<i>R</i>	0.999	0.999
	<i>N</i>	13	18
	concentration	20.8 \pm 0.2 mg/g	26 \pm 2 mg/g
	literature values	10–80 mg/g (36–38)	7–97 mg/g (36)
sugar-free cola A	volume added	150 μL	300 μL
	slope	0.2644 $\mu\text{A } \mu\text{M}^{-1}$	-0.2597 $\mu\text{A } \mu\text{M}^{-1}$
	<i>R</i>	0.989	0.999
	<i>N</i>	13	13
	concentration	502 \pm 26 mg/L	53 \pm 1 mg/L
	standard method result	385 mg/L	42 mg/L
sugar-free cola B	volume added	100 μL	150 μL
	slope	0.1171 $\mu\text{A } \mu\text{M}^{-1}$	-0.1660 $\mu\text{A } \mu\text{M}^{-1}$
	<i>R</i>	0.989	0.977
	<i>N</i>	10	10
	concentration	1083 \pm 176 mg/L	45 \pm 14 mg/L
	standard method result	383 mg/L	43 mg/L
sugar-free lemonade A	volume added	200 μL	200 μL
	slope	0.0950 $\mu\text{A } \mu\text{M}^{-1}$	-0.1712 $\mu\text{A } \mu\text{M}^{-1}$
	<i>R</i>	0.997	0.958
	<i>N</i>	10	10
	concentration	1175 \pm 124 mg/L	168 \pm 27 mg/L
	standard method result	154 mg/L	75 mg/L
sugar-free lemonade B	volume added	200 μL	200 μL
	slope	0.1284 $\mu\text{A } \mu\text{M}^{-1}$	-0.2017 $\mu\text{A } \mu\text{M}^{-1}$
	<i>R</i>	0.981	0.992
	<i>N</i>	10	10
	concentration	745 \pm 186 mg/L	59 \pm 10 mg/L
	standard method result	372 mg/L	90 mg/L
sugar-free lemonade C	volume added	150 μL	100 μL
	slope	0.1040 $\mu\text{A } \mu\text{M}^{-1}$	-0.1985 $\mu\text{A } \mu\text{M}^{-1}$
	<i>R</i>	0.981	0.989
	<i>N</i>	10	10
	concentration	466 \pm 125 mg/L	124 \pm 27 mg/L
	standard method result	323 mg/L	87 mg/L
sugar-free apple juice	volume added	150 μL	200 μL
	slope	0.0846 $\mu\text{A } \mu\text{M}^{-1}$	-0.2322 $\mu\text{A } \mu\text{M}^{-1}$
	<i>R</i>	0.985	0.999
	<i>N</i>	13	18
	concentration	1496 \pm 217 mg/L	70 \pm 10 mg/L
	literature values	317 mg/L (32)	4.5 mg/L (32)

^a *R*, correlation coefficient; *N*, the number of standard additions employed. The concentrations are quoted as the concentration \pm the 95% confidence interval.

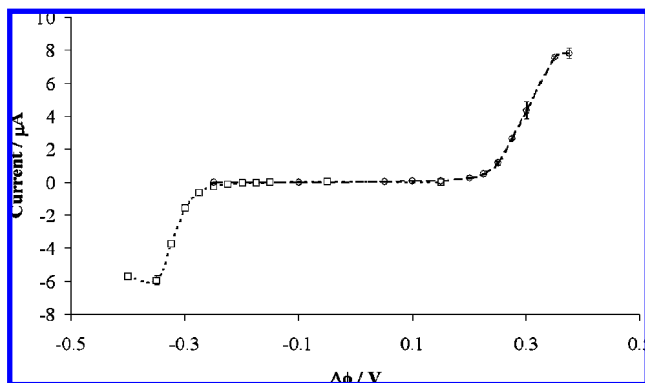


Figure 6. HDV of aspartame extraction (○) and acesulfame K extraction (□). Electrochemical cell 3.

This low extraction efficiency may be explained by the experimental cell design. The volume of the chamber in which the aqueous phase flows has an overall volume of 1.13 mL, which is 10 times greater than the volume of sample injected

(100 μL). It must be noted that the liquid–liquid extraction cell presents a high volume-to-area ratio, which leads to only a small fraction of the sample in contact with the organic gel phase. Furthermore, a flow rate of 1 mL min⁻¹ was selected to avoid distortion of the potentiostatic extraction peak. Although these experimental parameters limit the extraction efficiency, it has been demonstrated that selective extraction of aspartame and acesulfame K is possible, and with optimization of cell design and conditions, improved extraction efficiencies can be achieved.

Aspartame and acesulfame K were also extracted from the sugar-free cola using the same experimental setup. Potentials between 0.0 and +0.7 V (vs Ag–AgCl) were applied to monitor the extraction of ionic species from the cola (**Figure 7**). At 0.7 V (vs Ag–AgCl), the charge of aspartame extracted reached 72.5 \pm 0.9 μC . The quantity of aspartame injected in the flow analysis system, using the aspartame concentration calculated earlier, is 1.705 \times 10⁻⁷ mol. The resulting extraction efficiency is 0.4%, which is slightly lower than obtained for a clean laboratory-prepared solution of aspartame. The postextraction

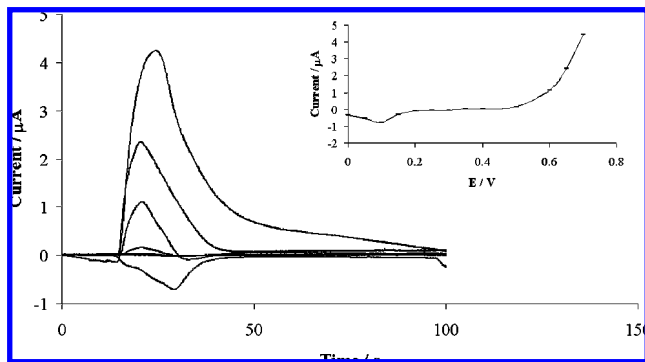


Figure 7. Potentiostatic extraction of aspartame and acesulfame K from sugar-free cola at potentials $E = +0.1, 0.4, 0.5, 0.6, 0.65,$ and 0.7 V (vs Ag–AgCl) from bottom to top. Inset: HDV of aspartame and acesulfame K extraction from sugar-free cola. Electrochemical cell 3.

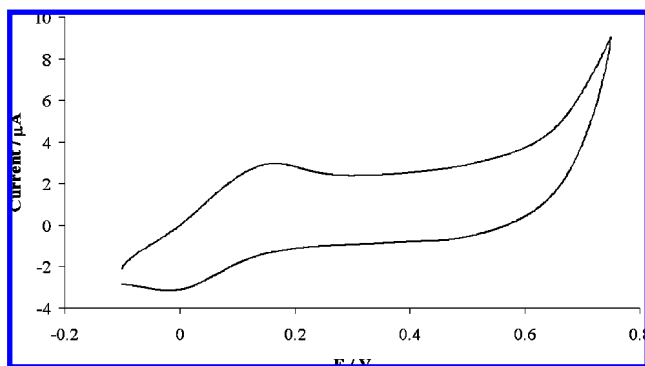


Figure 8. CV analysis of acesulfame K extracted at $+0.1$ V (vs Ag–AgCl). $\nu = 5$ mV s^{-1} ; electrochemical cell.

CV analysis demonstrated that acesulfame was indeed extracted from the beverage into the organogel (**Figure 8**).

From the above investigations, it can be seen that aspartame and acesulfame K were detected by ion transfer voltammetry at the liquid–liquid interface. Aspartame was also detected by facilitated ion transfer using the ionophore dibenzo-18-crown-6 but not in mixtures with acesulfame K, as potassium from that salt also transferred at similar potentials. The concentrations of acesulfame K were determined in food and beverage samples without the need for a prior sample preparation step. Preliminary investigation suggests that electrochemically modulated liquid–liquid extraction may be useful as a sample preparation strategy for these foodstuffs and analytes.

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