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Laser-based dynamic surface tension detection for liquid chromatography by probing a repeating drop radius

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Abstract

Modifications to the design of the time-based dynamic surface tension detection (DSTD) system are reported. Both a theoretical and experimental evaluation of the modifications are presented to demonstrate a reduction in flow-rate fluctuation derived systematic noise. The instrument-based limit of detection in relative surface tension change for the improved volume-based DSTD is determined to be 0.15% (3 × root-mean-square noise) as compared to the 0.45% level achieved and previously reported for the time-based method. The radius-based limit of detection for the drop is determined to be 0.5 μm, and may be limited by the vibrational stability of the drop. Detector selectivity is shown to remain unchanged after the modifications as only the observed noise levels are affected. Limits of detection for a variety of commercially available surfactant solutions are presented, along with those for a number of common organic and ionic chromatographic mobile phase modifiers, in order to demonstrate the enhanced selectivity of the DSTD for surface active species. The utility of the volume-based DSTD is demonstrated for the detection of trace intermediate to high molecular mass impurities in a high concentration low molecular mass surface active polymer matrix by comparing the response of refractive index and volume-based dynamic surface tension detection of a Carbowax sample analyzed using size-exclusion chromatography.

1. Introduction

The selective detection of surface active species is of interest for many analytical applications, such as the synthesis of polymeric surfactants, the monitoring of waste effluent streams, and in a wide array of manufacturing processes. Physical interactions of the polar and non-polar functionalities that comprise and characterize surface active species with the bulk solvent result in the preferential migration of these analytes to the surface, where due to energetic and entropic considerations, concentrated surface layers are formed. The concentration of surfactants at an air–liquid interface can be 10^5 times greater than in the bulk solution [1], and can result in a dramatic change in the surface tension of the solution. It is this physical property of surfactants that has made them useful as emulsifiers, flow improvers, and solution stabilizers [2–5] in the production of pesticides, cosmetics, soaps and detergents, food products, and vast collection of other commercially available products [6–8].

Surface tension is traditionally measured by one of a number of classical physical chemistry methods, such as by drop weight [9–13] or by use of the Wilhelmy plate [14–16], under static conditions [17–25]. These static methods require time for equilibrium conditions to be met and

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are impractical for use in a real-time laboratory or process analyzer. The novel time-based dynamic surface tension detection (DSTD) apparatus developed by Cronan [26] and characterized by Lima III et al. [27] shows promise in this regard. Based upon relating changes in the rate of detachment of drops suspended from a capillary tip to changes in the surface tension of a solution, the time-based DSTD allows for selective and sensitive detection of surface active species in real time. Use of the time-based DSTD apparatus under analytical conditions has promise for the analysis of weight-to-weight part-per-million (ppm) levels of surfactant species in solution, but use of the current detector configuration can be problematic due to the sensitivity of the time-based DSTD apparatus to flow-rate fluctuations. Presently, flow-rate fluctuations manifest themselves as changes in system surface tension and are the major source of systematic noise. The instrument limit of detection (LOD) for the time-based DSTD has been reported as being 0.45%, which is the LOD of the relative surface tension change [27].

An improvement in detector design will be reported in this manuscript. A laser beam with dimensions much smaller than that of the drop radius is used to probe the physical dimensions of the drop surface. Rather than infer drop volume changes from the rate of drop detachment, changes in the radius of the growing drop are measured. As such, we present the volume-based dynamic surface tension detector. A treatment of the signal response of the detector is presented in relation to previously reported theory in order to provide a means to quantitatively compare the two detector configurations. It will be shown that because drop volume is being measured directly, rather than inferred from drop rate, that the sensitivity to flow-rate fluctuations has been reduced for the volume-based DSTD apparatus. With this improvement the instrument detection limit for volume-based DSTD will be shown to be 0.15% and analyte limits of detection on the order of 1 ppm are observed for commercial products such as Carbowax 1450 (1450 g/mol nominal molecular mass). With a more complete evaluation of the calibration curve presented in our previous report [27] a factor of four improvement in LOD over the time-based method is reported. A preliminary analysis of two commercial soaps is presented, as well as the LODs for a number of species that are not surface active, including some common organic and ionic chromatographic mobile phase modifiers. Because the fundamental basis for detection has not changed by measuring the physical dimensions of the drop, as will be shown in the direct relationship between the theoretical basis for the signal response of the two methods, the volume-based DSTD apparatus is shown to retain the selectivity benefit of the original time-based configuration. Insensitivity to common mobile phase additives suggests that the volume-based DSTD apparatus holds promise for use with high-performance liquid chromatography (HPLC) or flow injection analysis (FIA). Lastly, Carbowax 200 (200 g/mol, nominal molecular mass) is examined by size-exclusion chromatography (SEC) with the volume-based DSTD apparatus in series and following a refractive index (RI) detector, to demonstrate the utility of the volume-based DSTD apparatus for the detection of trace intermediate molecular mass impurities in a concentrated low molecular mass matrix. It will be shown that volume-based DSTD offers a dramatically different view of Carbowax 200 than does RI detection. The combination of high selectivity for surface active components and high sensitivity makes the volume-based DSTD ideal for use as a quality control detector for the production of surface active polymers.

2. Theory

For the sake of clarity, we distinguish a description of the bulk solvent with a subscript of 1, the analyte with a subscript of 2, and a mixture with the subscript 1,2. From a fundamental point of view, changes in surface tension, $\Delta\gamma_{1,2}$, relative to some baseline surface tension, as caused by the presence of a surface active species are related to changes in drop

volume, $\Delta V_{1,2}$, relative to some baseline drop volume as shown by

$$\frac{\Delta\gamma_{1,2}}{\gamma_1} = \frac{\Delta V_{1,2}}{V_1} \quad (1)$$

From a combination of the treatment of surface tension of a two-phase system as reported by Connors and Wright [1] and a the classical drop weight method of surface tension determination presented by Adamson [10], the response of the time-based DSTD, $S(t)$, as described in our previous report [27] is defined as an indirect measure of relative changes in drop volume and given by

$$S(t) = \frac{\Delta V_{1,2}}{V_1}(t) = \frac{\Delta t_{1,2}}{t_1}(t) = C_2\left(\frac{t_1}{t_{eq}}\right)\frac{M_1}{10^6 M_2}\beta K_2\left(\frac{\gamma_2}{\gamma_1} - 1\right) \quad (2)$$

where t_1 is the baseline drop interval for the solvent, C_2 is the concentration of the analyte near the surface as observed at the detector, t_{eq} is defined as the time required for the solution to reach equilibrium under static conditions, M_1 and M_2 are the molecular masses of the solvent and analyte, respectively, β describes the relative geometry of the analyte, K_2 is the surface binding constant for the analyte, and γ_1 and γ_2 are the coefficients of surface tension for the solvent and analyte, respectively. Thus, the detector signal is defined as a combination of three contributions, relative change in surface tension, relative degree of surface activity, and transport of the surface active species to the air–liquid interface [27].

Similar to RI detection, the volume-based DSTD requires an absolute change in the probed physical property. The term $(\gamma_2/\gamma_1) - 1$ describes this absolute change in surface tension and is the basis for detection. However, the selectivity and enhanced sensitivity for surfactants depends upon the degree of surface activity of the analyte. Species that are surface active tend to form surface layers at which the concentration of the surfactant can be 10^5 greater than in the bulk solution [1]. From Connors and Wright [1], the term βK_2 combines the ability and tendency of a species to form and maintain a concentrated surface layer to describe the relative surface activity of an analyte. Thus, βK_2 describes the selectivity of dynamic surface tension detection. The final consideration in the basis for a signal response is the transport of the analyte to the surface by means of both convection and diffusion. From our previous report [27], the concentration of the analyte at the surface can be described by

$$\frac{ADC_2 t_1}{V_{SL}\delta} = C_2(t) \quad (3)$$

where A is the surface area of the interface, D is the effective translational diffusion coefficient of the analyte, V_{SL} is the volume of the surface layer, and δ is a diffusion distance characterized by the various transport mechanisms. Because a dynamic process is being examined, and because C_2 is fundamentally determined as the concentration of the analyte at the surface under equilibrium conditions, a relationship between the time scales of the two methods, dynamic and static, is needed. $C_2(t)$ is defined as unbound relative to the adsorption phenomena that occur at the surface, where $C_2(t) < C_2$. The equilibrium signal is defined when t_1 equals t_{eq} and $C_2(t)$ equals C_2, and the linear approximation is

$$C_2(t) = \frac{t_1}{t_{eq}} C_2 \quad (4)$$

where t_1 in practice with the DSTD is generally less than t_{eq}. Thus, the term $C_2(t_1/t_{eq})$ describes the transport of the analyte to the surface and relates the determination of surface tension by static and dynamic methods.

Let us consider Eq. 1 in more detail, to discover how to minimize the noise in the DSTD function. Time-based DSTD assumes a constant flow-rate, F, and since $V = Ft$, then the change in drop time, $\Delta t_{1,2}$, relative to a baseline drop time can infer the relative change in drop volume, as given by

$$\frac{\Delta V_{1,2}}{V_1} = \frac{F\Delta t_{1,2}}{Ft_1} = \frac{\Delta t_{1,2}}{t_1} \quad \text{(constant } F\text{)} \quad (5)$$

However, even with a high-quality pump with a

pulse dampener there are short term fluctuations in flow-rate that introduce noise to the system as these fluctuations manifest themselves as drop volume changes. While keeping t_1 constant, Eq. 5 is rewritten

$$\frac{\Delta V_{1,2}}{V_1} = \frac{\Delta F t_1}{F t_1} = \frac{\Delta F}{F} \quad (\text{constant } t_1) \tag{6}$$

and it is observed that changes in F are detected as apparent changes in t_1. It will be shown that flow-rate fluctuations directly affect the measured signal as noise. Flow-rate fluctuations do not greatly affect t_1 in terms of the transport of the analyte to the surface, as described by Eq. 3, but are a major source of baseline noise. The instrument LOD for the time-based DSTD apparatus, as defined as 3 times the root-mean-square noise, has been reported as 0.45%, and can be attributed to fluctuations in flow-rate. Furthermore, while flow-rate may drift a few percent per hour with a poor pump, one might anticipate severe baseline drift with the time-based DSTD method, whereas measuring $(\Delta V_{1,2})/(V_1)$ directly should perform substantially better.

Volume-based dynamic surface tension detection is based upon probing a length dimension of the drop and making a direct relation of changes in drop volume to changes in surface tension. If the geometry of the drop is assumed to be spherical, for the sake of simplicity, then the volume of the drop can be described by $V_1 = (4\pi/3)\, r_1^3$, where r_1 is the radius of the drop when only the solvent is present. The spherical assumption need not be entirely valid to achieve an acceptable model for the volume measurement. If we let $\Delta V_{1,2} = V_1 - V_{1,2}$ so that $V_{1,2} = V_1 - \Delta V_{1,2}$, then following Eq. 2

$$S(t) = \frac{V_{1,2}}{V_1} = \left(\frac{r_{1,2}}{r_1}\right)^3 \tag{7}$$

If $\Delta r_{1,2} = r_1 - r_{1,2}$ then

$$\frac{V_{1,2}}{V_1} = \left(\frac{r_1 - \Delta r_{1,2}}{r_1}\right)^3 = \left(1 - \frac{\Delta r_{1,2}}{r_1}\right)^3 \tag{8}$$

Since $(1+x)^n$ can be approximated by $1 + nx$ for small x, then we can approximate that

$$1 - \frac{\Delta V_{1,2}}{V_1} = 1 - \frac{3\Delta r_{1,2}}{r_1} \tag{9}$$

and thus,

$$S(t) = \frac{\Delta V_{1,2}}{V_1} = 3\left(\frac{\Delta r_{1,2}}{r_1}\right) \tag{10}$$

The term $3(\Delta r_{1,2}/r_1)$ therefore describes the instrument-based LOD when $\Delta r_{1,2}$ is determined from measuring the radius of successive drops, and when $\Delta r_{1,2}$ is three times the standard deviation of the drop dimension. In general $3(\Delta r_{1,2}/r_1)$ is the relative volume change, and thus the signal for the DSTD can be described by combining Eqs. 2 and 10 as

$$S(t) = \frac{\Delta t_{1,2}}{t_1}(t) = \frac{3\Delta r_{1,2}}{r_1}(t) = C_2\left(\frac{t_1}{t_{eq}}\right)\frac{M_1}{10^6 M_2}\beta K_2\left(\frac{\gamma_2}{\gamma_1} - 1\right) \tag{11}$$

The direct relationship between the time- and volume-based detection methods allows for a quantitative comparison of the instrument-based detection limits. Selectivity and sensitivity of the two methods should be equal, but the improvements in noise levels gained from volume-based detection allow for greater detectability and detector reliability.

3. Experimental

3.1. High-performance liquid chromatography (HPLC)

The experimental apparatus is shown in Fig. 1. 100% HPLC-grade water was used as the base mobile phase for all chromatographic and FIA analyses. Analytes consisted of sodium dodecylsulfate (SDS), a series of poly(ethylene glycol) molecular mass standards with molecular masses from 200 to 22 000 g/mol, samples of Dawn dishwasher detergent and Dial hand soap purchased from a local supermarket, HPLC-grade methanol and acetonitrile, phosphoric acid, sodium hydroxide, and a series of Carbowax samples (nominal molecular mass range

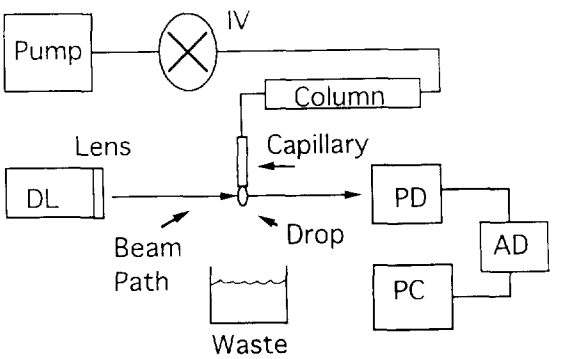

Fig. 1. Schematic of the volume-based dynamic surface tension detection (DSTD) apparatus: DL = diode laser with attached focusing lens; PD = photodiode; AD = data acquisition board; PC = personal computer; Pump = syringe pump; IV = injection valve; Column = size-exclusion column and pulse dampener. A pinhole type mask, not shown for clarity, is positioned between the suspended drop and the photodiode and used to block light that is not relevant to the detection.

of 200 to 8000 g/mol) (Union Carbide, Danbury, CT, USA). All solutions were sonicated thoroughly prior to introduction to the analyzing system. Analytes were introduced to the system using an injection valve (Rheodyne, 7520, Cotati, CA, USA) fitted with either a 10-μl (for FIA) or 100-μl (for HPLC) injection loop. The injection valve was connected to a RI detector (BioRad, Model 1670450, Hercules, CA, USA) using a short length of 1/16 in. O.D. × 0.005 in. I.D. (1 in. = 2.54 cm) poly(ether etherketone) (PEEK) tubing. For experiments involving a chromatographic separation a 2 mm × 250 mm column with 9-μm Asahipak (Keystone Scientific, Asahipak, Bellefonte, PA, USA) packing was inserted in place of this tubing length. Another short piece of PEEK tubing was used to contain the flow output from the RI detector. Into the open end of this piece of tubing a 0.33 mm O.D. × 0.20 mm I.D. glass capillary was inserted and secured using an epoxy. Drops from this capillary tip have a radius of roughly 1000 μm and a volume of approximately 6 μl. The tubing–capillary assembly was mounted using a clamp on a vertical post and connected to a X-Y-Z stage micrometer (Newport, 460 X-Y-Z, Fountain Valley, CA, USA).

3.2. Detector

A 670-nm diode laser (Lasermax, Rochester, NY, USA) was positioned 6 cm from the output of the capillary tip. The output from the laser was focused by means of a lens incorporated into the laser down to a 400 μm high by 200 μm rectangle such that the smaller beam dimension was placed in the horizontal growth axis of the drop. A pinhole type mask with a 0.5 cm radius hole was positioned 9 cm from the capillary tip and was used to block light not relevant to the detection mechanism. A photodiode array was positioned 4 cm behind the mask, and covered to block out any sources of stray light. A diagram of the relation between the drop, probe beam, and mask from the point of view of the laser is shown in Fig. 2, although not drawn to relative scale. The photodiode was interfaced to an amplifier/voltage offset box and then to a personal computer (Delphi, 80486-33, Seattle, WA, USA) via a data acquisition board, and to a chart recorder. Raw data was collected at 3000 points/s, and was smoothed by a 300 collected point/data point running average. The processed data consisted of a measure of the final radius growth of the drop, represented as an intensity voltage,

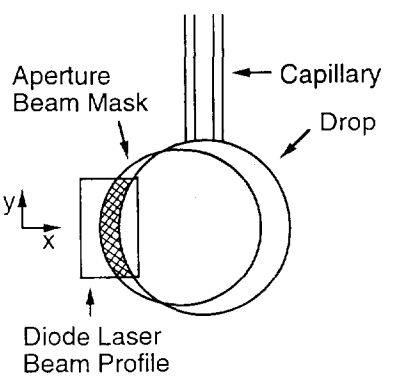

Fig. 2. Close-up schematic of the relationship between the focused laser profile, shown as the rectangle, the drop (shaded) and the pinhole mask, shown as the open circle. Light relevant to detection is shown with cross-hatching. Calibration of the intensity–drop radius relationship is performed by moving the drop along the x-axis, shown, into the beam profile until the beam is completely blocked. The beam width, not drawn to scale, is actually about 15% of the drop radius.

which was converted to $S(t)$ using Eq. 11 and the detector calibration data, as will be described. Additionally, the drop rate (time method) was simultaneously performed as in our previous report [27]. Using the translational stage, the drop was moved into the path of the beam so that a calibration curve relating drop radius to intensity voltage could be determined. All analyses were performed in the linear portion of the radius–intensity calibration curve. The detector system was optimized for the detection of small changes in relative drop radius, with a range on the order of 150 μm, or about 15% of the drop radius as the dynamic range. Since the drop dimension was substantially larger than the probe beam dimension, to a good approximation the detector simply measures changes in drop radius along the x-axis in Fig. 2. For the examination of flow-rate fluctuations, measurements of both baseline and analytical behavior were made with and without the chromatographic column in the flow line.

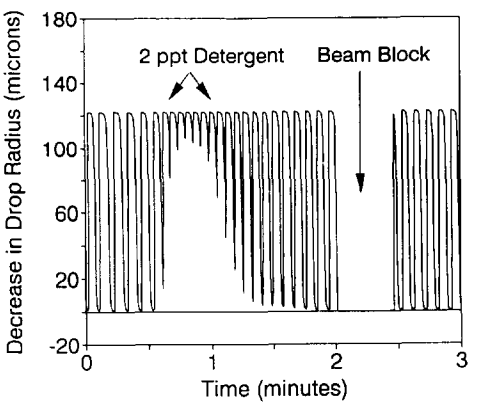

Fig. 3. Raw data collected at 4 points/s for the FIA analysis of a solution of 2 ppt Dawn liquid dishwasher detergent in water as observed by the volume-based DSTD method. The signal for complete beam blockage represents the position for the maximum baseline growth of the drop, labeled as 0 μm in the decrease of the drop radius. Analyte detection is observed as a decrease in the final radius of the drop, resulting in an increase in observed light intensity. The 2 ppt Dawn solution in water is shown to cause a 120 μm decrease in the radius of drop growth, from an initial radius of about 1000 μm for water.

4. Results and discussion

The volume-based DSTD apparatus works by monitoring the radial dimension of the repeating drop and measuring the changes in the intensity of the light that is blocked by the drop surface. Raw data, collected at 4 points/s, that demonstrates the basic principles of detection is presented as Fig. 3. Under baseline operating conditions, the repeating drop grows to a radius of about 1000 μm. As the drop grows, light that is normally transmitted to the photodiode detector is partially blocked, resulting in a loss in intensity observed at the detector. The intensity observed at the maximum radius of the drop was calibrated as a function of the linear position of the drop within the beam, and then the drop was positioned so that the beam would be almost completely blocked at full growth. At this position, the detector is optimized for radius changes on the order of 100 μm. From Fig. 3 it is observed that the intensity of the beam observed at the detector changes over the last 120 μm of the growth of the drop, and at full drop growth nearly all the light is blocked by the surface of the drop as is observed by the intensity observed when the beam is completely blocked by a solid mask. Due to the influence of a surface active species, in this case 2 ppt of Dawn liquid detergent in water, the surface tension of the system decreases. This surface tension decrease manifests as a change in final drop volume, and therefore a decrease in the radius of the drop. Since the drop now grows to a smaller final volume, the intensity of the light that is no longer obstructed by the drop surface increases. For the experimental conditions used, 10 to 50 drops typically define a surface active component peak, and the raw data peak for Dawn liquid detergent clearly shows a change in the surface tension of the drop system. For most experimental conditions, the raw data is processed during the data collection and only the maximum radius of drop growth is collected. The raw data is processed during collection using a program written in-house that collects the raw data at 3000 points/s and runs a 300 point/processed

point average over the raw data to determine the final maximum radius of drop growth.

Concurrently with the intensity data, the interval between repeating drops is recorded, so data for both the time-based and volume-based methods are collected simultaneously. This allows for a direct comparison of the two detection methods as explained in Eq. 11. Presented in Fig. 4 are the DSTD signals, following Eq. 11, for a FIA examination of a solution of 15.6 ppm Carbowax 1450 in water using a flow-rate dampener to minimize flow-rate fluctuations. Both data sets were smoothed by a 5-point running box car average and offset from zero for clarity. Detector signal was converted first from intensity voltage to drop radius in microns using a calibration curve what relates observed intensity to the position of the drop, as mentioned previously. From Eq. 9, radius changes can be converted to volume changes by dividing the radius signal, $\Delta r_{1,2}$, by the baseline radius of the drop, r_1, and multiplying the resulting value by 3. The instrument LOD of $S(t)$ for the time-based method of 0.45% from our previous report was determined from 3 times the root-mean-square noise of $\Delta t_{1,2}/t_1$ data. The instrument LOD of $S(t)$ for the volume-based method was determined by converting the radius data to the relative volume change equivalent as described in Eqs. 10 and 11. The standard deviation of $\Delta r_{1,2}$ was determined to be 0.16 μm for a radius change LOD of 0.5 μm with a baseline drop radius of 1000 μm. Thus, the instrument LOD of $S(t)$ for the volume-based method is determined to be 0.15%, representing a factor of 3 improvement in the amount of noise as compared to the time-based method. The smallest detectable radius change is limited by the vibrational stability of the drop. After removing the pulse dampener, the standard deviation in $S(t)$ for the noise levels for the volume- and time-based methods were once again determined, and are presented in Table 1. The instrument LOD for the time-based method increased by 60% as a result of the increase in flow-rate fluctuations caused by the removal of the pulse dampener, while the instrument LOD for the volume-based method remained unchanged. The enhancement of the volume-based method is even greater, as the time-based method is sensitive to not only flow-rate fluctuations, but also flow-rate drift as observed somewhat in Fig. 4. The volume-based DSTD is insensitive to gradual flow-rate drift, and demonstrates a net factor of four improvement in analyte detection. The limits of detection for a variety of species, including surfactants, organic and ionic chromatographic mobile phase modifiers, and non-surface active species is presented in Table 2. Note that a 1 ppm LOD is now observed for

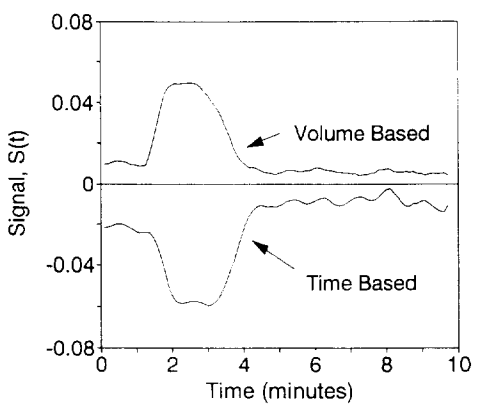

Fig. 4. Simultaneous collection of the DSTD data by volume- and time-based methods for a solution of 15.6 ppm Carbowax 1450 in water for comparison of signal response and relative noise levels. The volume-based (upper data set) data represents a decrease in the final radius of the drop while the time-based (lower data set) data represents a decrease in the time interval between successive drops. Both data sets are smoothed by a 5-point boxcar average, and are offset by a value of 0.01 from their respective baselines at a signal value, $S(t)$, of 0. Noise levels for the volume-based data are a factor of 3 less than for the time-based data. The sensitivity of both methods is equivalent as represented by the equal signal heights.

Table 1
LOD of $S(t)$ from noise levels determined for time- and volume-based DSTD methods with and without pulse dampener, in signal units

	With dampener	Without dampener
Volume-based DSTD	0.0015	0.0015
Time-based DSTD	0.0045	0.0072

Table 2
LODs for a variety of surfactants, non-surfactants, and common chromatographic mobile phase additives, as observed in water

	LOD (ppm)
Surfactants	
Poly(ethylene glycol) 1450	1
Poly(ethylene glycol) 7100	2
Sodium dodecylsulfate	1
Dawn liquid detergent	8
Dial liquid hand soap	8
Non-surfactants	
Poly(ethylene glycol) 200	1000
Ethylene glycol	10 000
Mobile phase modifiers	
Methanol	500
Acetonitrile	500
1 m*M* NaOH	–[a]
1 m*M* H_3PO_4	–[a]
Water (blank injection)	–[a]

[a] Not detectable.

PEG 1450, as compared to the 4 ppm LOD determined for PEG 1470 in our previous report [27]. Improvement in the sensitivity of volume-based DSTD is observed for sodium dodecylsulfate (SDS) as compared to our previous report. Ionic surfactants can be used to titrate non-ionic surfactants resulting in decreased surface activity in the pairing, and we believe the presence of PEG in solution led to the determination of an artificially high LOD for SDS in our previous report. Insensitivity of the volume-based DSTD to common organic and ionic mobile phase modifiers, as well as for non-surface active species, demonstrates that the selectivity of the detector has not been affected by the modifications to the experimental design. In addition, these results suggest that the volume-based DSTD apparatus would be well suited for use with HPLC and FIA.

To demonstrate this utility, an application of the volume-based DSTD apparatus in an industrial product evaluation and using SEC is presented. The ability to detect intermediate to high molecular mass impurities in high concentration low molecular mass matrices is a concern in the synthesis of surface active polymers. Using an RI detector and volume-based DSTD apparatus in series we performed a SEC analysis of a commercial sample of Carbowax 200, composed of poly(ethylene glycol) (PEG) with a nominal molecular mass of 200 g/mol. From previous reports, we have determined the sensitivity of the PEG series as a function of molecular mass and have shown that PEG 200 is not highly surface active [27]. Fig. 5A shows the RI response for a 1% solution of Carbowax 200 in water collected at 2 points/s and after smoothing by a 30-point boxcar average. One peak appears, and according to our calibration of the SEC as presented in a previous report the molecular mass of that peak corresponds roughly to PEG 200 [28]. The retention volume positions for PEGs of increasing molecular mass are shown. Fig. 5B shows the response for the volume-based DSTD apparatus in conjunction with that for the RI detector. From the volume-based DSTD apparatus, two peaks appear with severe overlapping of the second and smaller peak by the first. From the retention volume data in Fig. 5A, the second peak in Fig. 5B corresponds to the detection of PEG 200, however the first, and more sensitively detected peak possesses no refractive index counterpart. Subsequent analysis of a series of PEG molecular mass standards and comparison to the retention calibration curve in Fig. 5A for the size-exclusion column suggests that the peak corresponds to that expected for PEG 1250. While the sensitivity of the two species using RI detection is nearly equivalent, PEG 1250 is approximately 200 times more sensitive than PEG 200 using the DSTD. From the calibration series determined for PEG 1450, a similar species, the concentration of PEG 1250 detected is on the order of 200 ppm in the original sample and 20 ppm at the detector. The use of the volume-based DSTD apparatus has substantially improved the diagnostic capability in this analysis.

The performance of the new volume-based DSTD apparatus is shown to possess a factor of four enhancement over that of the time-based DSTD apparatus design. Detection limits of the order of 1 ppm are observed for surface active species, while the selectivity of the detection remains enhanced for surface active species.

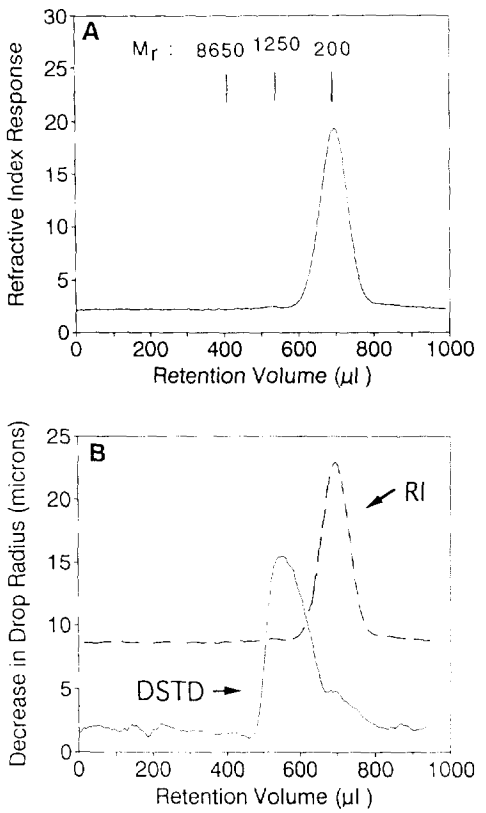

Fig. 5. (A) RI detection of a 1% solution of Carbowax 200 as analyzed using size-exclusion chromatography. The retention volume positions, as determined from a calibration of the column by higher molecular mass (M_r) PEG species is indicated, yet only the peak for PEG 200 is observed. (B) Overlay of the sequentially and simultaneously collected RI and volume-based DSTD detector responses. A small peak representing the minimally surface active PEG 200 is observed, but is severely overlapped by a peak for an analyte that is tentatively identified as the surface active species, PEG 1250. RI detector sensitivity for the two species is equivalent, but substantial enhancement for the detection of the surface active higher molecular mass species is observed using volume-based DSTD. From calibration curves for a similar species, PEG 1470, the concentration of the PEG 1250 peak is approximately 20 ppm at the detector which is consistent with not observing the impurity in the RI chromatogram.

Insensitivity of the volume-based DSTD apparatus to organic and ionic mobile phase modifiers suggests that the detector is promising for use with HPLC or FIA. Analysis of two commercially available soaps is performed to show the utility of the detector for analysis of complex mixtures. Lastly, the combination of selectivity for surfactants and sensitivity is demonstrated for the detection of intermediate molecular mass surface active species in more concentrated low molecular mass, non-surface active matrices with implication towards use for the synthesis of surface active polymers.

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