

Chip-based Polyaniline and Gold Nanoparticles Modified Electrode for Determination of D-glucosamine in Pharmaceutical Products

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In this work, a novel screen-printed carbon paste electrode based on gold nanoparticles (Au-NPs) incorporated with polyaniline (PANI), a well-known conductive polymer, was presented for determination of D-glucosamine, a dietary supplement for osteoarthritis. The amounts of Au-NPs, PANI and pH of a working solution were optimized using the central composite design (CCD). Results demonstrated that the optimum concentrations of Au-NPs and PANI were 300 ppm and 3 mg/mL, respectively. A suitable pH of working solution was found to be pH 4. The mass transfer of the modified electrode defined a diffusion-controlled process at low concentrations of analyte while an adsorption-controlled process was observed at high concentrations of analyte. Two dynamic ranges of 2.5-40 mM and 40-100 mM were obtained with R^2 values equal to 0.9966 and 0.9984, respectively. Limit of detection (LOD) and limit of quantitation (LOQ) were equal to 0.67 and 2.24 mM, respectively. Compared with the conventional high performance liquid chromatography (HPLC) method using a gold plate electrode for determination of D-glucosamine, this method makes a great promise for analysis of D-glucosamine because it is simple, fast, portable, robust and inexpensive for pharmaceutical analysis and could be applicable for on-site measurements. Further applications of this modified electrode will be focused on quantitative determination of D-glucosamine in real samples. In addition, this system will be applied for a microfluidic system to expedite analysis to be a high throughput manner.

Keywords D-glucosamine; Polyaniline; Gold-nanoparticles; Electrochemical detector; Central composite design

References

1. Charoenraks, T., Chuanuwatanakul, S., Honda, K., Yamaguchi, Y., Chailapakul, O., 2005, *Anal. Sci.*, 21, 241-245.
2. Pashkova, E., Pirogov, A., Bendryshev, A., Ivanaynen, E., Shpigun, O., 2009, *J. Pharma. Biomed. Anal.*, 50, 671-674.
3. Tominaga, M., Nagashima, M., Taniguchi, I., 2006, *Electrochemistry Communications*, 9, 911-914.
4. Fernandez, E., Vidal, L., Iniesta, J., Metter, J.P., Banks, C.E., Canals, A., 2014, *Anal. Bioanal. Chem.*, 406, 2197-2204.

Bloodstain Age Estimation from Color Substrates using a Smartphone and Digital Image Analysis

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The ability to determine the time since deposition of a bloodstain found at a crime scene could prove invaluable to law enforcement investigators. However, no reliable methods are currently available for this purpose. A low-cost system based on digital image analysis of photographs of bloodstains obtained from a smartphone camera was previously described, but the color of the background interfered with the process. In this study we improved upon the previous method by incorporating a color extraction step. Bloodstains from four donors were deposited on four color substrates and extracted using phosphate buffer saline solution with vigorous vortexing. The extracted solutions were then photographed with a Sony Xperia Z and the color values (RGB, CMYK, and HSV) of each pixel were determined using ImageJ. Interdonor comparison was performed and the environmental effects including temperature, humidity, light and anticoagulant were investigated. Color values obtained from the digital images were correlated with bloodstain age, with magenta having the highest correlation ($R^2 = 0.886$). No difference between bloodstain donors were observed, but temperature, humidity, light, anticoagulant and substrate influenced the aging process. The change in bloodstain color is consistent with the hemoglobin degradation process and agrees with previous studies. The incorporation of the extraction step enables bloodstains on colors substrates to be analyzed and has the potential to be used on-site, while the system costs only a fraction of other techniques such as HPLC or hyperspectral imaging.

Keywords Bloodstain age estimation; Color substrate; Bloodstain color extraction; Digital image analysis

References

1. Thanakiatkrai, P., Yoadam, A. and Kitpipit, T., 2013, *Forensic Sci. Int.*, 233, 288-297.
2. Bremmer, R. H., de Bruin, K. G., van Gemert, M. J.C., van Leeuwen, T. G. and Aalders, M. C.G., 2012, *Forensic Sci. Int.*, 216, 1-11.
3. Bremmer, R. H., Nadort, A., van Leeuwen, T. G., van Germert, M. j.C. and Aalders, M. C.G, 2011, *Forensic Sci. Int.*, 206, 166-171.

Colorimetric Determination of Nitrite and Nitrate in Meat using Paper-based Analytical Device (PAD)

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Nitrite and nitrate have also been used as food additives using in processed meat to prevent the spoilage, kept the meat red and produce the good smell. They are food contaminants that as a result of degenerative diseases that effects on human health at high levels caused of Eutrophication, Methemoglobinemia and cancer. Paper was chosen as the substrate for preparing these devices, which they have been shown to be effective testing for a simple, rapid, inexpensive and easy-to-use. A simple colorimetric method for the detection of nitrite and nitrate using paper-based analytical device (PAD) is reported in this work. These Griess reaction can be applied for the determination of nitrite while nitrate was reduced to nitrite on PAD in the section of hydrophilic channel coated with zinc dust. The optimal conditions for the determination of both nitrite and nitrate including the concentration of N-(1-naphthyl)-ethylenediamine dihydrochloride (NED) and sulfanilamide, reaction time, as well as three patterns of PAD were studied. Under the optimal conditions, the color intensity gave a linear response in the range 0-20 mgL⁻¹ ($R^2 = 0.993$ for nitrite and $R^2 = 0.981$ for nitrate) and the limits of detection was found at 0.1 mgL⁻¹. The purple color in the presence of nitrite and nitrate can be clearly observed in PAD (pattern 1) by the naked eye within 25 minutes. Moreover, our PAD was applied for the determination of nitrite and nitrate in real samples such as poke sausage, smoked poke sausage, and ham.

Keywords Colorimetric method; Griess reaction; Nitrate; Nitrite; PAD

References

1. Jayawardane, B. M., Wei, S., McKelvie, D. I. and Kolev, D. S., 2014, *Anal. Chem*, 86, 7274–7279.

Chemometrics and LIBS Applied to Forensic Science for the Elucidation of False Wine Stamps

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Laser-induced breakdown spectroscopy (LIBS) is an analytical technique that allows for the determination of a sample's elemental composition based on laser ablation followed by atomic, ionic, and molecular emission processes coming from elements transferred into the plasma as a result of laser-induced breakdown. Recent advances in instrumentation have produced commercially available LIBS spectrometers that are inexpensive compared to instrumentation required for comparable techniques. Characteristics of LIBS, including rapid analysis time, lack of required sample preparation, potential for field portability, and cost effectiveness, make this relatively non-destructive method of analysis very attractive for forensic applications.

In this work, 23 tax stamp samples from liquor bottles were analyzed using the LIBS instrument: 15 authentic samples and 8 false samples. The samples were collected by the civil police of São Paulo State during oversight operations. Two different regions from each sample were analyzed: a region containing a hologram and a region of blank paper (without paint). From the LIBS results, a $\mathbf{X}_{23,1565}$ matrix was constructed for the data region containing the hologram and another, with the same dimension, for the data of the blank paper region (without paint). The total number of rows corresponded to the number of samples and columns corresponded to the wavelength. After this, PCA and HCA chemometric methods were used. The second part of the work was the classification of samples through PLS-DA chemometric method. For this, the spectra of all samples were arranged in $\mathbf{X}_{\text{calibration}}$ matrix (14 x 1565) and in $\mathbf{X}_{\text{validation}}$ matrix (8 x 1562). Thus, the calibration and validation sets were constructed with 14 spectra (10 spectra of authentic samples and 4 spectra of false samples) and 8 spectra (4 spectrum of authentic samples and 4 spectra of false samples), respectively. This procedure was performed for the construction of the PLS-DA model with the samples in the region of the hologram and for the data obtained for the region of blank paper. The use of chemometric techniques with the LIBS technique was able to identify the authentic and false samples in wine stamps. Thus, the proposed methodology can be used by authorities and by the police for identification of wine stamps in a fast, cheap and non-destructive way.

Keywords LIBS; Chemometrics; Forensic sciences

PIXE, PIGE and Backscattering Spectrometry as Analytical Techniques

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Chemists are confronted with a range of analytical techniques and consequently utilize an increasing number of methods based on physical, biological and chemical sampling. The primary aim of the analytical chemist is to solve a problem in a most expeditious route. Therefore, for an analytical technique to be accepted in the practical world, it must compete favorably with all the other methods in the arsenal of the analyst. A method will also find wide acceptance if it provides unique advantages in areas of selectivity (the range of elements which can be analyzed), sensitivity (limits of detection (LODs) - the minimum amount of the element that can be detected, linearity (the concentration range that can be used in an analysis), speed of analysis (how quickly a determination can be effected), matrix effects (the influence of other elements in the specimen matrix on the determination of a particular element) and multi-elemental applicability (the determination of elements sequentially or simultaneously). Many present day techniques such as Flame Atomic Absorption Spectrometry, Inductively Coupled (Argon) Plasma-Atomic Emission Spectrometry and Laser Ablation are based on dissolution, that is, destructive specimen preparation. There is therefore a need for techniques that offer non-destructive analytical capability. The paper provides an overview of how the non-destructive analytical techniques of Particle-Induced X-ray Emission spectrometry, Rutherford Backscattering Spectrometry and Particle-Induced gamma-ray Emission spectrometry, collectively denoted as Ion Beam Analysis (IBA) can be used complementarily to each other and utilized simultaneously. Emphasis is placed on the use these unique IBA advantages in the determination of elements, especially C, N, O, P and S. Through this means, a range of applications are found, especially in establishing the elemental concentration distribution in various specimens. The paper provides, amongst others, correlation between the element LOD and the atomic number in IBA, and the application of these techniques in the chemometric characterization of superconducting materials.

Keywords Proton induced x-ray emission; Backscatter spectrometry; Proton induced gamma-ray emission; Chemometrics; Minimum detection limits

Zone-Fluidic Manipulation by Sequential Injection for the Analysis of Octanol–Water Partition Coefficient of Drugs

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It is demonstrated in this work that sequential injection (SI) can be effectively manipulated in handling of microliter-volumes of two immiscible fluids for liquid-liquid extraction. The on-line SI extraction was then employed to develop a new procedure for measuring the so-called 'octanol-water partition coefficient' (P_{OW}) of drugs. Generally, P_{OW} describes the capability of transportation of a drug through cell membrane. The P_{OW} can be measured by determining the concentration ratio of drug partitioned in octanol zone and water zone at equilibrium ($P_{OW} = C_O/C_W$). In the SI system, microliters of octanol (4.2 μ L), phosphate buffer saline (4.2 μ L) and drug sample were aspirated into a holding column (200 μ m i.d.). We found that this holding column must be placed in a vertical position in order to achieve the complete separation of the two phases. In this method, absorbance measurements in only one phase (octanol or aqueous) were used for calculation of the P_{OW} . The detection wavelength was set to the maximum absorbance wavelength for each drug. The efficiency of the system was tested with some commercial drugs with known P_{OW} . Good correlation of this method with a batch method ($r^2 = 0.999$) and literature value ($r^2 = 0.997$) was obtained.

Keywords Octanol-water partition coefficient; Sequential injection; Lipophilicity

References

1. Karin, C., Bo, K., 2000, *Anal. Chim. Acta*, 423, 137-144.
2. Thorsten, H., Johannes, S., 2004, *Drug Discovery Today: Technologies*, 1, 431-439.
3. Panwadee, W., Phoonthawee, S., Prapin, W., Duangjai, N., Saowapak, T., 2014, *Anal. Chim. Acta*, DOI: 10.1016/j.aca.2014.08.025

Determination of Arsenolipids in Marine Foods

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Arsenic in its inorganic forms (iAs) is a known toxic element, and iAs present as a natural component of drinking water in many countries worldwide has been implicated in major detrimental health effects including cancers and cardiovascular disease. Arsenic also occurs in many foods, particularly those of marine origin, but in this case iAs is usually a minor part of the total arsenic content, with almost all the arsenic being present as organoarsenic compounds considered to be non-toxic. Over the last seven years, however, several studies have shown that many marine foods also contain a new class of organoarsenicals comprising lipid-soluble compounds termed arsenolipids. The properties of these arsenolipids are very different from those of other organoarsenic compounds previously identified in foods, all of which have been water-soluble. Indeed, recent cytotoxicity studies have revealed that three of the six arsenolipids tested so far showed cytotoxicity comparable to that of iAs. The presentation will discuss analytical methods based on HPLC-ICPMS-orbitrap MS for the identification and quantitative determination of arsenolipids in food items.

Keywords Arsenic; Food; Mass spectrometry

Trace Analysis of Cd (II) Ion using PSDVB-EDTA as Material Column Filler in Pre-concentration Technique with Off-line Method

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The trace analysis of Cd (II) ion used polystyrene divinyl benzene-ethylene diamine tetraacetate (PSDVB-EDTA) as the material column filler in pre-concentration technique with off-line method has been done. The pre-concentration method was performed by a column filled with PSDVB-EDTA activated at pH 6 with sodium acetate. The optimal conditions for the best analytical performed in pre-concentration steps were 9 mL injection volume of water samples and 3 mL of 1.0 M HCl as eluent. The obtained retention capacity was 6.44 mg/g Cd(II) /g resin. The analytical performance of the method was very good; the limit of detection values was 3.85 µg/L. The reproducibility value expressed as percentage of coefficient variance was 4.1%. This method provided good accuracy in term of good recoveries in the range of 5 to 100 µg/L without the effect of interferences in real water sample. The proposed method can certainly analyze Cd (II) in water samples at the trace levels.

Keywords Cadmium (II); Trace analysis; Pre-concentration; PSDVB-EDTA

References

1. Amran, M. B dan Heimbürger, R., 1996, *Fresenius J. Anal. Chem.*, 354, 550-556.
2. Amran, M.B., A.S. Panggabean, A. Sulaeman and M. Rusnadi., 2010, *Int. J. Environ. Res.*, 5, 531-536.
3. Karadas, C., D. Kara dan A. Fisher., 2011, *Analytica Chimica Acta*, 689, 184-189.
4. Panggabean, A.S., Pasaribu, S.P., Bohari, and Nurhasanah., 2014, *Indo. J. Chem.*, 14, 51-56.

Dispersive Liquid-Liquid Microextraction Followed by Gas Chromatography for Determination of Four Phthalate Esters in Water Samples

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Dispersive liquid-liquid microextraction (DLLME) was developed for the extraction of four phthalate esters; dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP) and di(2-ethylhexyl) phthalate (DEHP), in small scale of water samples and analyzed by gas chromatography. The important parameters such as type and volume of extraction solvent and dispersive solvent, extraction time and salt addition effect were investigated. Under the optimum extraction conditions, the linearity was observed over the range of 10-5,000 $\mu\text{g L}^{-1}$ for DMP and 5-5,000 $\mu\text{g L}^{-1}$ for DEP, DBP and DEHP in the initial solution with correlation coefficients (R^2) in the range of 0.990-0.999. The limits of detection (LOD) of method were 35.88-53.37 $\mu\text{g L}^{-1}$. The method was successfully applied to analyze four phthalate esters in water samples. The percentage recoveries were above 80% in all samples.

Keywords Phthalate ester; Preconcentration; Dispersive liquid-liquid microextraction; Gas chromatography

References

1. Farahani, H., Norouzi, P., Dinarvand, R. and Ganjali, M. R., 2007, *J. Chromatogr. A*, 1172, 105-112.
2. Panagiotou, A. N., Sakkas, V. A. and Albanis, T. A., 2009, *Anal. Chim. Acta*, 649, 135-140.

Pros and Cons of the Schlieren Effect in Flow-Based Analysis and Its Application in Analysis of Sugar Contents of Food and Beverage Syrups

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Schlieren effect is the phenomenon of light refraction at the boundary of two liquids with different refractive indices. The signal profile arising from this phenomenon often perturbs the measurement of light absorption in spectrometry. Albeit the ‘Cons’ of the schlieren effect in flow-based analysis, there is a ‘Pros’ side to this effect, since the schlieren signal correlates with the concentration of a solute in the solution. In this work, utilization of the schlieren effect is demonstrated for the quantitative analysis of sugar content in food and beverage syrups. After dilution with water (1:50), the sample (50 μ L) was injected into a stream of water (flow rate, 2 mLmin⁻¹). To avoid absorption of the sample in UV-Vis region, the light source was selected in the near-IR range (890 nm). Linear calibration (Absorbance = [(3.34 \pm 0.05) \times 10⁻²] \cdot Brix + [(0.13 \pm 0.06) \times 10⁻²]; $r^2 = 0.999$), was successfully obtained from 0.2 -2.0 Brix with extremely high sample throughput of 180 injections h⁻¹. Applications of the method to food and beverage syrups gave results that corresponded well with reference method using a refractometer.

Keywords Schlieren effect; Sugar; Syrup

References

1. Teerasong, S., Chan-Eam, S., Sereenonchai, K., Amornthammarong, N., Ratanawimarnwong, N. and Nacapricha, D., 2010, *Anal Chim Acta*, 668, 47-53.
2. Mantim, T., Saetear, P., Teerasong, S., Chan-Eam, S., Sereenonchai, K., Amornthammarong, N., Ratanawimarnwong, N., Wilairat, P., Meesiri, W., Uraisin, K., and Nacapricha, D., 2012, *Pure Appl. Chem.*, 84, 2015–2025.
3. Saetear, P., Khamtau, K., Ratanawimarnwong, N., Sereenonchai, K., and Nacapricha, D., 2013, *Talanta*, 115, 361-366.