HPLC2008

32nd International Symposium on High Performance Liquid Phase Separations and Related Techniques, May 10-16, Baltimore, MD, USA

HPLC2008 took place between Sunday, May 11th to Friday, May 16th at the Marriott Waterfront Hotel, Baltimore, USA under the Co-Chairmanship of Profs, Georges Guiochon and Steve Jacobsen. With in excess of 900 delegates registered, this premier symposium series in separation science remains buoyant despite the general adverse economic climate and the less than favourable conditions being experienced by the pharmaceutical industry. Delegates attending peaked in the middle days while the exhibition was running but, at the opening plenary session over 400 delegates had arrived and even at the closing session on Friday morning approaching 250 hardy souls had held out to the very end. 420 posters were presented, just a slight drop on the previous year's meeting in Belgium.

With much of the meeting being run in three parallel sessions it was only possible to catch up with a fraction of the many high quality oral presentations. However, as ever, this event captured the thrust of where the main action was taking place in separation science. There was standing room only for sessions on column technology themes such as sub-2 micron particles, superficially porous particles, monoliths and 2D-separations.

These topics were also covered in very useful tutorial and discussion sessions and the first two of the topics also featured strongly in the lunchtime vendor seminars. The tutorial and discussion sessions involved some backtracking over old work and overlap with other presentations but nonetheless went down very well, serving as a vehicle to hear first-hand the career highlights of the great and the good in separation science (e.g. Klaus Unger, Pat Sandra, Peter Carr, Peter Schoenmakers) and to help focus on the current key issues. Notably, there were lots of nodding heads when Klaus Unger wound up his tutorial with a statement that great advances had been made in improving resolution through higher efficiency with new stationary phase technology and now it was time to revisit selectivity.

There wasn't too much evidence of this in HPLC2008 but maybe this will be how things go for HPLC2009 and 2010?

'Dr John Lough (President of The Chromatographic Society) presents Dr Ron Majors with the 2007 Martin Gold Medal'

Given the interest in column technology issues, the sessions actually entitled "Advances in Column Technology" drew a large proportion of the delegates. The first speaker in the first of these was Ron Majors, Agilent Technologies, Inc, who the day previously had been awarded the Martin Gold Medal of The Chromatographic Society for his outstanding contributions to the development of separation science. Ron's talk on "HPLC Column Technology: Smaller and Faster" was wide-ranging but distinguishable from other presentations featuring superficially porous particles by the focus on the value of Agilent's Poroshell materials for protein separations. The point was made that given that the optimum linear velocity is lower for large molecules than for small molecules because of their slower diffusion rates, the shorter diffusion distances in e.g. Poroshell 120 are beneficial. The next speaker Jack Kirkland, Advanced Materials Technologies Inc, addressed very similar technology i.e. his company's fused core silica. Importantly, as well as highlighting e.g. the narrow particle size distribution, he touched upon an obvious potential weakness, that of loadability. He presented data determined with a peak of $k = 3$ to demonstrate that the loading capacity was more than satisfactory. Calculation of the total pore volume available revealed that this is higher than might have been expected. Also, given that the loadability is not that much reduced from that of totally porous 3-µm particles, it is possible that in LC using the latter' the analyte molecules do not diffuse deep into the particles. Kirkland mentioned the HILIC mode of LC and David McCalley, the following speaker (who like Ron Majors had received a Chromatographic Society award (the Jubilee Silver Medal) the day previously) moved things completely into this territory with his presentation on work carried out on 'naked' silica. Amongst other issues, David discussed (a) the strong C term that had been observed (possibly due to external roughness on the particle) when using a HALO shell particle silica column, (b) his estimation of the volume of the water 'layer', and (c) the what he called "new" advantages of high linear velocities due to the use of low viscosity solvents and the ability to overload ionic solutes (10x loadability) *cf* when using an RP partition mechanism. For the final talk in this session, given by Monika Dittman, Agilent, matters reverted to speed and efficiency aspects of fused core / superficially porous particles. More specifically, comparisons were made with totally porous particles in the context of the van Deemter coefficients using a modified term for intraparticle diffusion and with special reference to the relationship between the C terms and *k*.

The second session on Advances in Column Technology included one of the few presentations that addressed the issue of stationary phase selectivity. Frank Dorman, Restek, recognising this, by the time he gave his talk on Wednesday, had inserted Unger's tutorial quotation on selectivity into his own presentation! Much of "unique selectivity" claimed arose from a new range of aryl stationary phases with a biphenyl phase seeming to give the most interesting selectivity and aliphatic spacers allowing greater loadability. "Tanaka test probes" were used as a tool to study the selectivity. One possible drawback from this type of work is that, while the analytes used are selected specifically to probe for a particular type of interaction and thereby differentiate between phases, the phases deemed to be 'different' by the probes may not necessarily show differences in the analysis of 'real' analytes (which are not, by their nature, optimised probes). In the context of the general thrust of the symposium it was worth noting that the phases described were designed for use in "UHPLC".

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Chromatography Focus

Dr David McCalley, Chromatographic Society 2008 Jubilee Silver Medal Winner, addresses the audience in Baltimore

Technically, the session on chiral separations could also be considered as part of the column and stationary phase technology focus but the content represented the continuing evolutionary development of a mature field rather than revolutionary breakthroughs. Wolfgang Lindner presented his work on chiral ion-exchangers. This represents an excellent body of research which is perhaps undervalued only because of what has gone before it in the field. It was however not too easy to discern what was introductory background information and what was new. Irving Wainer has frequently observed chiral differentiation in his work on cellular membrane affinity chromatography. In his talk here at Baltimore he chose to focus on the resolution of D,L-methorphan on an AChR channel column, paying particular attention to the mechanism for chiral resolution and in so doing triggering off a debate with the previous speaker. Chiral micro-emulsion electrokinetic chromatography (MEEKC) also featured in this session. This is without doubt a methodology for chiral resolution that has missed its time. However, it has to be said that an excellent, comprehensive presentation on the topic was given, starting with a strong theoretical background which looked as though it had been extrapolated out of the work of Steve Wren on MEKC. Fifteen chiral analytes were studied and, impressively, data from all eight combinations from the three possibilities for the introduction of chirality (oil, surfactant, co-surfactant) was presented.

The heavily over-subscribed lunchtime vendor seminars played an important role in the symposium. Their high attendances might have had a little to do with the free lunches on offer and the fact that most days the weather outside was somewhat inclement, but there were some exciting new products being featured. For example, Shimadzu launched their new HPLC system which is not only designed for U-HPLC but also can deliver high enough flow to also be used for conventional LC. Also, Doug McCabe of Waters described a new range of column chemistries that his company have introduced to build upon the success of their previous developments in UPLC. Of course, these new product developments were also on display at the exhibition. Again, this was well integrated into the symposium. The exhibition hall was shared with some of the poster presentations and coffee and snacks were served during intervals. The exhibition was very much geared towards the USA market. While this would not be ideal e.g. for any international delegate with an imminent purchase in mind, it is unavoidable in such meetings.

The symposium finished with presentations and welcomes to the next three meetings in the HPLC series. The best poster prize, sponsored by Agilent, went to Gert Desmet's group from Belgium. "The Future of HPLC and UPLC: Are Higher Pressures and Smaller Particles Opportune?" was presented by Ken Broeckhoven. The runner-up poster "Application of Fused-Core Particle Technology in the Separations of Natural Product and Related Impurities" was presented by Peilin Yang of The Dow Chemical Company, USA. The third rated poster was "Comparison of Detection Techniques for LC x LC Separation of Natural Compounds in Beverages" was presented by Petr Cesia of the Czech Republic. Thanks were accorded to Ron Majors who, after exactly a decade in charge, was

L to R; David McCalley (University of the West Of England)), AidrianClarke (Astra Zeneca, UK) and Bang Lu enjoy the Baltimore Highlife.

handing over the chairmanship of the poster prize judging committee to Gerard Rozing and Peter Schoenmakers. The Pfizer prizes for best posters relating to pharmaceutical analysis were not only pleasingly 'orthogonal' to the Agilent awards with the emphasis being on innovation rather than overall quality of poster but also biologically orientated with prizes for work on on-line coupling of monolithic enzyme reactors, affinity LC on a GPR17-recepror column and 2D protein separations. HPLC Inc, a company set up by American members of the HPLC Permanent Scientific Committee, were responsible for the Csaba Horvath prize for best oral presentation by an up-and-coming separation scientist. The highly deserving winner was Jude Abia, University of Tennessee who gave a very lucid presentation on his work on the radial homogeneity of silica-based wide-bore monolithic columns. As per tradition, the symposium closed with invites to forthcoming meetings in the series. Look out for the satellite meeting in Kyoto, December 2nd – 5th, 2008 (Chair: Nobuo Tanaka), Dresden, June 28th – July 2nd, 2009 (Chair: Christian Huber) and Boston, June 19th – 24th, 2010 (Chair: Steve Cohen).

Not to be forgotten amidst the closing activities were tributes to Janet Barr and George Guiochon. Janet Cunningham's PCO company Barr Enterprises has been responsible for successfully staging many of the HPLC symposia held in the USA. Co-chairing this event with Steve Jacobssen, this was the third HPLC meeting that Prof. Guiochon has organised. He certainly showed that by now he knows how to make a good job of it!

Solvent Enhanced Light Scattering GPC Technology

Viscotek has been a strong advocate of good chromatography as a prerequisite for GPC (Gel Permeation Chromatography) data accuracy. Their recent work in application development has been driven by extremely difficult samples from industrial, biopharmaceutical and academic sources. These samples present challenges ranging from sample solubility, column adsorption as well as detection issues. Utilising sample and mobile phase solvents with the proper dilution and injection, they have been able to increase the dn/dc value to get better LS response. This type of analysis is Solvent Enhanced Light Scattering (SELS) GPC.

Circle no. 10

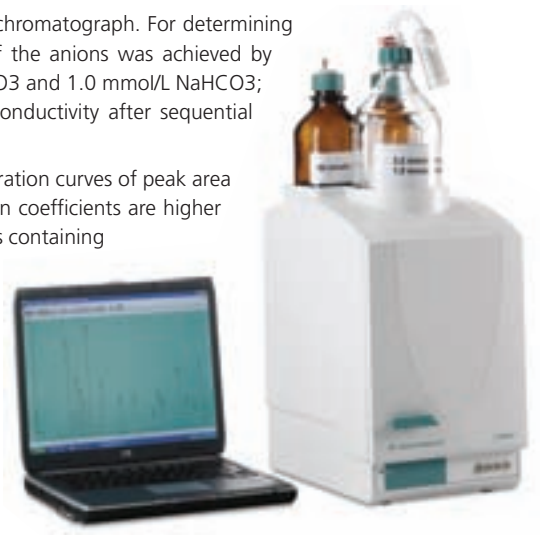
Determination of Sulfate in Denatured Ethyl Alcohol by Direct Injection IC

In times of skyrocketing gasoline prices, ethanol fuel is a promising renewable high-octane vehicular fuel. A major drawback, however, is the contamination with inorganic salt ions such as chloride, nitrate and sulfate. These ions can affect the engine performance because precipitating salts clog filters fuel injector nozzles. Furthermore, these ions enhance corrosion in the vehicle components in contact with the fuel. Hence there is an urgent need for standards defining quality specification and test methods. While the analysis of sulfate is specified in a number of ASTM norms, until recently, the ASTM D 4806-06b standard – the specification for denatured fuel ethanol – provided no guidelines for total and potential sulfate. Recognising the need for validated methods for quality control, ASTM balloted and approved a sulfate specification for fuel ethanol stipulating a maximum level of sulfate in ethanol of 4 parts per million (ppm). The corresponding chloride contamination limit in ethanol is proposed at 40 ppm.

In this paper a convenient direct injection suppressed ion chromatographic method for determining chloride and sulfate in denatured ethanol samples is presented. The described method is the subject to the recent ASTM D 7319 and the results obtained fully comply with ASTM D 4806-06c. System setup: 861 Compact IC with 'MCS'; 'MSM II' **Metrohm** Suppressor Module (trichamber); 838 Advanced Sample processor; Metrosep A Supp 5 – 150; Metrosep RP Guard; and M-Pak® for A Supp 5.

The determination of inorganic sulfate and chloride in ethanol samples involves the direct injection of 20 µL ethanol into the ion chromatograph. For determining the potential sulfate, 0.5 mL of 30% hydrogen peroxide solution is added to 9.5 mL of the ethanol sample. Quantification of the anions was achieved by integration of the resulting peaks compared with an external calibration curve. Experimental conditions: Eluent - 3.2 mmol/L Na2CO3 and 1.0 mmol/L NaHCO3; column - Metrosep A Supp 5 – 150; column temperature - 35 oC; flow rate - 0.7 mL/min; sample size - 20 µL; detector - conductivity after sequential suppression; suppressor solutions - 100 mmol/L H2SO4 at 0.5 mL/min (regenerant) and high purity water at 0.5 mL/min

The determination of total and potential sulfate and inorganic chloride in fuel ethanol is the subject of ASTM D 7319. External calibration curves of peak area versus concentration are linear in the range 0.625…50 ppm for chloride and 0.25…20 ppm for sulfate. Corresponding correlation coefficients are higher than 0.9998 and the limits of detection for chloride and sulfate are 0.6 and 0.2 ppm, respectively. Even after 1500 ethanol injections containing denaturants and hydrogen peroxide, the analytical unit still provides stable retention times, repeatable peak areas and consistent concentration values. The excellent repeatability and reproducibility of the applied trichamber «MSM II» suppressor demonstrates its ruggedness in long-term use. For all investigated samples, standards and blanks, both mass spectrometric and conductivity detection provide accurate and precise results. The presented direct injection IC system is solvent compatible and ensures the accurate and precise determination of sulfate and other anions in ethanol samples in full compliance ASTM D 4806-06c.



Circle no. 11