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An assay procedure to compare sorptive capacities of activated carbon dressings: the detection of impregnation with silver

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Abstract—A semiquantitative assay procedure for the estimation of uptake of diethylamine by activated carbon dressings has been developed. The procedure involves the use of Nessler's reagent as a comparative indicator. The use of diethylamine allows the concomitant detection of silver with which the dressings may be impregnated. The implications of silver/amine complex formation during dressing use are discussed. Quantification of the silver content of one such fabric was carried out by atomic absorption spectrophotometry. A silver content of 2770 ppm was found. It is suggested that this method might be suitable for adoption as the basis for a pharmacopoeial assay procedure for activated carbon dressings.

Activated carbon in the form of a cloth (known as charcoal cloth) may be produced from a viscose rayon fabric that has been chemically pretreated and then carbonized at high temperatures in an atmosphere of nitrogen or carbon dioxide. The resulting material resembles the original rayon fabric in form, but is composed entirely of carbon together with residues of the material used for chemical impregnation before carbonization. A charcoal felt is also produced in this manner (Bailey et al 1973; Capon et al 1982).

Charcoal cloth has several industrial applications, not least among which are its medical uses, for instance, in surgical masks, flatus filters, and in wound management. In particular, the deodorizing properties of the material on maladorous lesions can provide welcome relief to both patients and nursing staff alike (Butcher et al 1976). Similarly, the ability of activated carbon to sorb bacteria (Frost et al 1980) is likely to be a contributory factor in the healing of infected lesions.

Several methods of assessing the activity of charcoal cloth have been described, the choice of any particular method being determined by the use to which the cloth is to be put. Thus, methods measuring dynamic adsorption of carbon tetrachloride, chlorobenzene, halothane, or other vapours from an airstream by measuring penetration time through a given number of layers of the cloth at a specified relative humidity and flow rate have been used, as have methods for measuring adsorption of dinitrophenol, styrene, benzaldehyde, phenol, dimethoate, and other materials from solution (Charcoal Cloth—undated, Siebe Gorman—undated). 'In house' methods of quality assurance include the measurement of the heat of wetting (see Atkinson et al 1982) by benzene (Charcoal Cloth—undated), or the sorption of phenazone from solution (Johnson & Johnson Ltd). This latter procedure is an adaptation of the European Pharmacopoeia method for the determination of the sorptive capacity of Activated Charcoal.

It is evident from published data that individual compounds are sorbed to markedly different extents—the saturation vapour adsorption of carbon tetrachloride, for instance, being 80% by weight whereas that of benzene is only 50% by weight (Charcoal Cloth, Technical Data, Charcoal Cloth Ltd). The general observation has been made that the degree of sorption is inversely related to the volatility (as measured by the boiling point) of any particular compound (Bailey & Hollingdale-Smith 1977). It is evident, therefore, that an assay procedure designed to quantify (or semi-quantify) the performance of activated carbon dressings should ideally measure uptake of material that is actually released from a malodorous wound. For social reasons, the use of compounds such as cadaverine or putrescine, diamines such as are released from necrotic tissue, is difficult to justify. A compromise was therefore sought when the use of diethylamine was considered. A method has been developed that involves the semi-quantitative assessment of the quantity of precipitate produced when Nessler's reagent is added to the liquor remaining after the immersion of a piece of the activated carbon fabric in a dilute aqueous solution of diethylamine.

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Materials and methods

Preparation of the activated carbon fabrics. Where appropriate, the activated carbon fabric was initially removed from the proprietary dressing product. A 3 cm × 5 cm piece of each sample was boiled with ammonia-free glass-distilled water for 15 min and reactivated in a preheated oven at 105°C for 1 h. When cool, each piece was weighed and stored at room temperature for 15 min.

Materials used were: (1) Charcoal cloth (Charcoal Cloth Ltd., Maidenhead, Berks UK), (2) Charcoal cloth (silvered) (Charcoal Cloth Ltd); (3) Charcoal felt on fabric backing (Charcoal Cloth Ltd/UK Health & Safety Executive); (4) Actisorb (Johnson & Johnson Ltd., Slough, Berks UK); (5) Bandor (ASTEC Environmental Systems Ltd, Bristol, UK); (6) Lyofoam C (Ultra Laboratories Ltd, Sittingbourne, Kent, UK); (7) W.O.W. Bandage BPC (Cuxson, Gerrard & Co. Ltd, Warley, West Midlands, UK).

Diethylamine solutions. From a pilot study, it was found that a concentration of diethylamine between 0·10 and 0·20% in ammonia-free water was appropriate to the sample size of activated carbon dressings to be used. Batteries of six 100 mL glass beakers each containing 25 mL of a diethylamine solution (0·10, 0·12, 0·14, 0·16, 0·18, & 0·20% v/v) were prepared from a 1·0% v/v stock solution.

Preparation of Nessler's reagent. Potassium iodide (61·75 g) was dissolved in 250 mL ammonia-free water (which had been previously boiled for 15 min and cooled). To this solution was added a cold saturated solution of mercuric chloride just sufficient to produce a permanent bright red precipitate. The precipitate was dissolved by the addition of 0·75 g potassium iodide. Potassium hydroxide solution (150 g in 250 mL ammonia-free water) was then added and the whole solution made up to 1 L.

Assay method. Two batteries of the six dilutions of diethylamine were used for each determination, one being used for control determinations. Six identical pieces of the material under test were cut and prepared as described above before being placed into the six beakers in the first battery. The beakers were allowed to stand for 15 min with occasional gentle swirling, then the

Table 1. Diethylamine sorption assay results.

	Weights* used (g)	Diethylamine conc (% v/v) Turbidity 0·10	0·12	0·14	0·16	0·18	0·20	Diethylamine sorbed (mL/100 g)
Control		1+	2+	3+	4+	5+	6+	
(1) Charcoal cloth	0·181	+	+	+	1+	2+	3+	8·3
(2) Charcoal cloth (silvered)	0·225	3+	4+	5+	6+	7+	8+	Indeterm
(3) Charcoal felt	0·394	+	1+	2+	3+	4+	5+	1·3
(4) Actisorb	0·202	+	+	+	+	+	1+	12·4
(5) Bandor	0·321	Dark coloured ppte						Indeterm
(6) Lyofoam C	0·191	+	+	1+	2+	3+	4+†	5·2
(7) W.O.W. bandage	0·106	1+	2+	3+	4+	5+	6+	0

* Mean weight of the six samples used per assay
† A yellow colouration was imparted to the test solution

pieces of dressing were removed from the solutions and carefully drained. To each beaker in the two batteries was added 2 mL Nessler's reagent and the degree of turbidity caused by the white precipitate thus formed in the control battery was compared on a 1+ to 6+ scale with that formed in the test battery.

The assay procedure was repeated until two concordant results were achieved for each product. In practice, only one duplicate experiment was required.

Assay of silver by atomic absorption spectrophotometry. A sample of each dressing material (4·0 g) was wet ashed in conc. nitric acid. The residue was taken up in 1% nitric acid and made up to 50 mL. Portions (25 mL) of these solutions were further diluted to 1 L.

Standard silver nitrate solutions containing 1, 2, 3, 4, 5, and 8 $\mu g\ mL^{-1}$ were prepared in 1% nitric acid from a 1 mg mL^{-1} stock solution obtained from BDH Chemicals, Poole, Dorset, UK (Spectrosol grade) and gave absorbance values of 11, 24, 35, 48, 60 and 90, respectively.

Samples were aspirated through an air/acetylene flame and assayed at 328 nm with a monochromator slit width of 0·2 mm using a Varian 1000 instrument. Background absorption was measured in the usual way using a hydrogen lamp.

Results and discussion

The diethylamine sorption results are in Table 1. The silver assay was negative for all the materials except the silvered charcoal cloth (2) for which an absorbance reading of 64 units was obtained. The equivalent to that of a solution with a silver content of 5·54 $\mu g\ mL^{-1}$. This solution had been prepared from a sample of charcoal cloth weighing 4·0 g that had been digested and made up to 2000 mL. The charcoal cloth (silvered) therefore contained

$$5{\cdot}54 \times 2000/4\ \mu g\ Ag\ g^{-1} = 2770\ ppm\ or\ 0{\cdot}28\%\ w/w.$$

Despite the relatively crude methodology, the assay procedure involving a semi-quantitative assessment of diethylamine sorption by activated carbon fabrics enabled a comparison of the various products to be made. The precision of the method would appear to be adequate when the use to which activated charcoal dressings are put is considered. However, because of the non-existence of a legally enforcable performance standard for these materials, the samples used may or may not be representative of currently used or available materials.

The diethylamine sorption assay enables some further information to be gained about the products. A dark brown colouration was imparted to the diethylamine solutions when the Bandor activated charcoal cloth was tested. This rendered the assessment of sorptive capacity inappropriate because of the subsequent adverse effect on the precipitate produced by addition of Nessler's reagent. It is presumed that the dark coloured precipitate was the result of an interaction between the diethylamine and residues of the impregnating solution used in the manufacture of the cloth. No attempt was made here to identify the cause of this reaction. The activated carbon material from Lyofoam C also produced a discolouration of the diethylamine solutions, but not sufficient to mask the readings after addition of Nessler's reagent. Charcoal Cloth (silvered) appeared to contribute diethylamine to the contents of the test beakers, since the quantity of precipitate produced by subsequent additions of Nessler's reagent was visibly greater than that produced in the control beakers. A spurious result was not entirely unexpected since silver is known to form co-ordination complexes with simple amines. Presumably, it was the formation of such a complex with the diethylamine in the test beakers that contributed to the increased turbidity observed. The presence of 2770 ppm silver in this product was determined by atomic absorption spectrophotometry. Calculations reveal that each 15 cm^2 sample of Charcoal Cloth (silvered) weighing 0·225 g contained about 0·63 mg silver (i.e. 0·28%). Assuming that the silver/amine complex is the $Ag[(C_2H_5)_2NH]_2^+$ ion, the 0·63 mg silver requires 0·853 mg diethylamine for complete reaction. Since the test beakers contained between 0·025 and 0·05 mL diethylamine, representing 0·018 to 0·035 g of diethylamine (d = 0·707), it would appear that there was a 20- to 40-fold excess of diethylamine available for reaction. The observed result suggests that much if not all the silver present in/on the fabric was leached away in a form that was not capable of being re-sorbed by the activated carbon, and formed a white Ag/amine/Hg/I complex when Nessler's reagent was added. The intensity of this precipitate evidently more than counterbalanced the loss of diethylamine/Nessler's reagent precipitate caused by sorption of diethylamine onto the activated carbon fabric.

Whilst no attempt was made to determine whether the unidentified coloured compounds were released from the activated carbon fabrics in response to the alkaline pH of the diethylamine solutions or whether they would be released into an amine-containing exudate from a skin lesion, all three of these cases could raise questions of safety in use in necrotic lesions containing significant quantities of diamines such as putrescine and cadaverine. It should be stated however, that all activated carbon fabrics in use in currently available wound management products are enclosed within other materials that would modify the final lesion/dressing interaction. It is also of relevance that an unreferenced claim is made in the advertising literature on a recently launched activated charcoal cloth with silver wound management product (Actisorb Plus, Johnson & Johnson Ltd) that 'the silver is chemically and physically bound to the

charcoal cloth and not released into the wound'—although the nature of either the chemical or the physical carbon-silver bonds in the '100% pure activated carbon with silver' is not stated.

Of the remaining four products, Charcoal Cloth appeared to sorb a smaller quantity of diethylamine than did Actisorb, whilst the charcoal felt sorbed only a little more than the W.O.W. bandage used as a control. The charcoal felt was actually bonded onto a layer of a white support material thus effectively lessening the available amount of activated carbon per unit weight of fabric. The W.O.W. bandage sorbed insufficient diethylamine to exceed the lower limit of detection of the assay procedure.

In summary, the assay procedure described here is apparently capable of differentiating between a number of activated carbon fabrics whilst also being able to provide a limited amount of incidental information regarding possible chemical reactivity at the wound/dressing interface.

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New method for testing the absorbency of surgical dressings

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Abstract—Absorbent cellulose dressings have been tested by immersion in a standard aqueous solution of picric acid followed by standard draining, elution of the picric acid, and measurement of the absorbance of the yellow colour at 355 nm. Six samples of gauze were graded by this procedure, and two considered unsatisfactory, despite all sinking in less than 10s. Filmated gauzes and unwoven dressings required greater dilution for the absorbance readings, reflecting their different structures.

Following World War I, the British Pharmaceutical Codex introduced monographs on surgical dressings. The 1923 Codex set the first standard for the absorbency of Absorbent Cotton Wool—"one gramme . . . compressed to a volume of about 20 mils, and dropped . . . on to the surface of distilled water at about 15° . . . should sink readily". The 1959 Codex applied a time limit, requiring it to be "saturated within ten seconds", in water now at 20°C, and extending the standard to Absorbent Gauze BPC. In practice, good absorbent dressings would saturate in a couple of seconds, whilst those that still complied by becoming saturated in 9 s were not much better in use than those that failed by taking 11 s.

The saturation testing of Absorbent Gauze BPC could be more closely prescribed by specifying its folding, and this was done in the 1973 Codex, but Absorbent Cotton Wool remained a problem to handle. The 1971 first European Pharmacopoeia, followed by the British Pharmacopoeia of 1980, introduced a container to standardize the procedure. About 5 g of the dressing, in a defined, lightweight wire basket, was required to sink in not more than 10 s; and then, on draining for 30 s, to show a water-holding capacity of not less than 23 g of water g^{-1} dressing.

Water-holding capacity probably does not reflect the ability of a dressing to absorb wound exudate, but it gives another numerical standard to support the saturation requirement. The possibility of grading absorbent dressings by the use of these tests has been ignored, apart from the water-holding capacity of Absorbent Cotton and Viscose Wadding reflecting its 40–60% content of cotton by requiring only not less than 20 g of water g^{-1} dressing. Viscose fibres have a lower water-holding ability (between the fibres?) than cotton, although they have a higher moisture regain ability inside the fibres.

Over 35 years ago Savage et al (1952) published their method for assessing the water retention coefficient of absorbent dressings. This has not been used officially, possibly because it involved wetting a test dressing which had been held by bandage to an inflated balloon. A range of coefficients was obtained, and these values were different for woven and unwoven cotton. Other techniques have included measuring the uptake of dextran in saline applied to the underside of a dressing—possibly under pressure (Williams 1975).

The need for an improved absorbency test seems apparent, and the possibility of using aqueous coloured solutions which could be measured by spectrophotometry suggested itself. These solutions have several properties required of their colour: (i) it must not react with the cellulose of the absorbent dressing fibres (cotton or viscose); (ii) it must be eluted readily and completely from the dressing under test; (iii) it must be easily washed out of glassware used for repeated testing; (iv) it must show a stable strong absorbance maximum when diluted in aqueous solution, unchanged after contact with cellulose fibres.

After considering a number of coloured substances, including phenol red, picric acid was chosen for the coloured solution since it had an absorption maximum at 355 nm and possessed the required properties, except that owing to its explosive nature when dry, it is supplied wetted. However, the initial arbitary solution of it can be standardized by dilution to give a required absorption reading for the *test solution* in use.

Materials and methods

Picric Acid (BDH)—50% by weight of water. Pye Unicam SP6-500 spectrophotometer.

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