ANALYTICAL METHODS

A simple method for estimation of newsprint dyes in effluents and their migration from paper samples

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ABSTRACT

An analytical method for the estimation of basic dyes, such as crystal violet (C.I. Basic Violet 3), malachite green (C.I. Basic Green 4), and methylene blue (C.I. Basic Blue 9), in newsprint effluents and water samples has been developed. Several solid-phase extraction (SPE) sorbents available for sample preparation have been evaluated for concentrating the dyes prior to analysis by high-pressure liquid chromatography (HPLC). Results show that only strong cation-exchange sorbents are capable of complete dye retention from newsprint effluents. However, a suitable eluent for the quantitative desorption of dyes from the strong cation-exchange sorbents was not found. All cation-exchange materials and some other sorbents retained dyes from dilute aqueous solutions. Unmodified silica was the most effective sorbent for recovering dyes dissolved in distilled water. Elution of dyes from the silica sorbent was achieved by countercurrent washing with a 1% solution of formic acid in aqueous methanol.

For estimation of the dyes in effluents, a qualitative test is proposed that involves sorption of dyes from effluents onto a silica-based cation-exchange sorbent and comparison of the resulting color band (if dyes are present) with a standard template.

Extraction results of newsprint samples in hot solvents show that, in water, no dye migrated from the paper.

Application:

Mill chemists can perform the test if the presence of the dyes in effluents is suspected.

IN THE PRODUCTION OF NEWSPRINT and lightweight coated (LWC) papers, basic dyes are used to suppress the yellow hue of unbleached and mechanical pulp fibers *(1, 2)*. The water-soluble dyes yield intensely colored cations and simple colorless anions upon dissociation in solution. The cations exhibit a high affinity for the acidic groups on the fibers. The majority of basic dyes used in Canadian newsprint mills are, according to the results of our survey, of the triphenylmethane structural type. This type of dye is also used for the coloring of textile fibers, such as modified acrylics and polyesters *(2, 3)*, for preservation of poultry feed *(4)*, and as topical antifungus treatments used now only on animals *(5)*.

Figure 1 shows structures of two frequently used triphenylmethane-type dyes and one thiazine type; the latter is also a newsprint dye but is not widely used at present. Basic dyes, especially those of the triphenylmethane type, are thought to be toxic to fish *(6)*. For example, recent results *(7)* and data in the literature *(8)* indicate LC_{50} values of cationic triphenylmethane dyes at about 0.2 mg/L or lower. Thus, it is important to be able to measure how much of these compounds is in effluents destined for discharge into receiving waters from industries using the dyes. A sensitive analytical method is required for such measurements, and it would entail preconcentration of the dyes from large effluent volumes. Since basic dyes are water soluble, classical liquid–liquid extraction with a water-immiscible solvent would not likely succeed. Rushing and Bowman *(9)* have shown that crystal violet cannot be recovered from wastewater using this approach. In the same report, solid-phase extraction (SPE) on an octadecyl silica sorbent as the extraction material was shown to recover 60% of the dye from spiked farm wastewater.

The presence of toxic dyes in newsprint and other paper products may be of concern to producers and end users. The ability of the dyes to migrate (bleed) from tinted paper products, under normal usage conditions, is a critical parameter in assessing the potential hazards of these compounds.

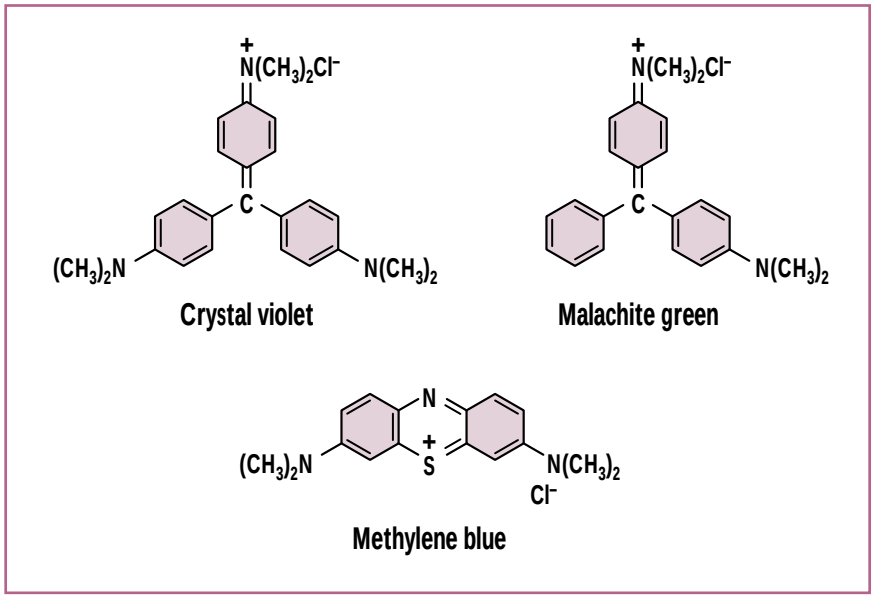
In this paper, we describe the development of a sensitive analytical method suitable for semiquantitative determination of dyes in newsprint effluents and water samples. We also discuss the results of potential migration of the compounds from newsprint samples into hot solvents.

EXPERIMENTAL

SPE sorbents

From a large variety of materials available for sample preparation, the following sorbents were evaluated for preconcentration of dyes from dilute aqueous and effluent solutions:

- A polymer-based strong cation-exchange resin, AG(R) 50W-X8 (H+), consisting of sulfonated crosslinked styrene/divinylbenzene copolymer (100–200 mesh size) was obtained from Bio-Rad Laboratories. The sorbent was received in open columns with a bed size that was 4 cm high and



1. The structure of some dyestuff cations. (Positive charges are delocalized.)

0.8 cm in diam., packed in distilled water (Cat. No. 731-6213).

- A silica-based strong cation exchanger consisting of silica particles (average diam.=40 µm, approx. 60 Å pore size) with bonded propylsulfonic groups on the surface was obtained from Supelco Inc. It was received in the form of extraction tubes (Supelclean LC-SCX, Cat. No. 52018), which were made of polypropylene bodies partially filled with dry packing (1.5 cm column height and 0.9-cm diam.) confined between two frits with 20 µm pores.
- Phosphorylated cellulose, P11 grade, in the monoammonium form and sulfoethoxycellulose, grade SE 53, in the sodium form were obtained from Whatman Specialty Product Division. SPE columns containing these sorbents were prepared as described in the "SPE procedures" section.
- A weak cation-exchange resin, consisting of a macroreticular acrylic polymer with bonded carboxylic acid groups (Bio-Rex 70, in sodium form) was purchased from Bio-Rad Laboratories. It was obtained as prefilled open columns, with a bed size that was 4 cm high and 0.8 cm in diam., packed in distilled water.
- Alumina B, silica, and the following silica-based bonded phases were also evaluated: octadecyl (C18), diol, and aminopropyl. They were obtained from Millipore Corp. in the form of SEP-PAK® cartridges (Classic type). They contained 360 mg of sorbent material in the group of silica-bonded phases, 690 mg of silica, and 1710 mg of Alumina B. The sorbent columns were about 2.3 cm long and 0.9 cm in diam., confined between two frits with 20 µm pores.

Procedures in SPE

The preconcentration testing was done on a mixture of three dyes, i.e., crystal violet (CV), malachite green (MG), and methylene blue (MeB). Dilute solutions of each dye mixture were passed through the SPE columns at a flow rate of 3–4 mL/min under a vacuum. As the dye solutions are colored, their sorption properties and desorption efficiencies of a variety of eluents were first estimated visually. Then, in some experiments, the actual recovery efficiencies were determined by measuring the dye concentrations in the eluates by high pressure liquid chromatography (HPLC).

Prior to use, prepacked columns and cartridges containing hydrophilic materials were rinsed with about 30 mL of distilled water, whereas hydrophobic sorbents (silica-C_{18}) were first conditioned with methanol and then with water. Dyes were then extracted from dilute solutions or from spiked effluents at neutral pH.

SPE columns containing cellulosic packings were prepared as follows. The lower portions of empty 3-mL Supelclean extraction tubes (Supelco Inc.) were cut to 2.5 cm above the bottom frit and packed under a vacuum with the dilute fiber suspension. Prior to packing, the cation-exchange sorbents were "cycled" according to the manufacturer's suggestions to remove impurities. This procedure consisted of contacting the sorbents with alkaline solutions, washing, contacting with acid solutions, washing, and finally leaving the suspension at a neutral pH. The column containers were filled with washed sorbents and then capped with the empty casings of SEP-PAK® cartridges, which happened to fit snugly over the Supelclean extraction tubes. According to the literature data on wet-packed densities and other properties *(10),* the containers would hold at least 0.15 g of cellulosic exchangers after slurry packing which, at the lowest exchange capacity (0.2 µeq/g for sulfoethylcellulose), corresponds to at least 30 µeq of exchangeable cations per column. In all subsequent SPE extractions from dilute solutions (< 1 mg/L), the amount of each dye to be sorbed was below 1 µeq.

To extract dyes from large volumes of solutions, a 250 mL separa-

tory funnel with a Teflon™ stopcock was fitted (through another piece of the Supelclean tube) to the cartridge containing SPE material and then connected to an evacuated flask. Dilute dye solutions were prepared by pipetting aliquots of standard mixtures (10 mg/L of each dye in methanol) into glass beakers containing water or mill effluent. Pyrex-grade pipettes and glassware were acid washed and thoroughly rinsed with distilled water prior to use. (Dyes tend to deposit on soft glass and on some plastics, e.g., that used in "B-D" Brand disposable syringes, but not those used in extraction tubes and cartridges.)

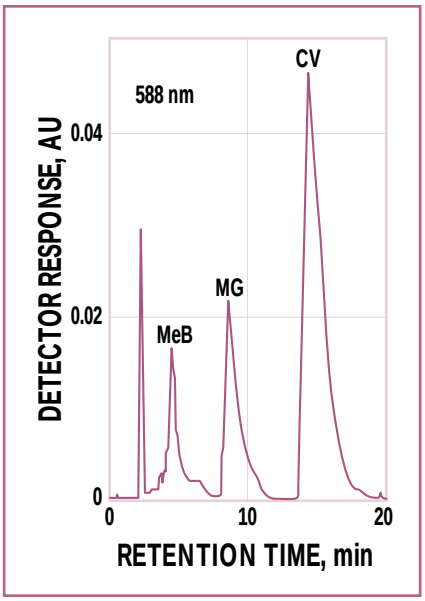
The dye solutions were dripped from the separatory funnel at a vacuum that was sufficient to give a flow of 3–4 mL/min through the SPE sorbent. In experiments with effluents, suspended solids were removed by sedimentation prior to the spiking step to avoid possible losses of dyes on solids and to minimize the plugging of frits. For this purpose, 0.7 L portions of effluents were centrifuged in 1 L Nalgene bottles for 30 min at 5200 Relative Centrifugal Force (i.e., *g*-value), and then 0.5 L aliquots were decanted into glass beakers. This procedure did not eliminate but greatly reduced the amount of solids, as indicated by the increased resistance of cartridges to the flow after several hundred milliliters of effluent had passed. Alternatively, effluents were filtered through millipore filters (8 µm pore size) in a Sartorius vacuum assembly. Filtration was very slow due to plugging. Moreover, filters were found to sorb the dyes, and thus this method of solids removal would not be suitable for extraction of dissolved dyes in effluents.

After the sorption step, SPE sorbents containing dyes were not washed prior to elution, since there were no coeluting compounds in eluates that interfered in HPLC analysis of dyes. The elution step of sorbed dyes is independent of the sorption step during preconcentration. However, as described in "Results and discussion," the ease of elution greatly depends on the sorbent. For sorbents where no interferences occurred in the sorption step, the dyes were concentrated in the top layers of the sorbent beds. When using cartridges containing such sorbents, reversed-flow elution is most effective. This was done slowly under positive pressure into a 15 mL graduated glass tube. After elution, the eluent volume was read (allowing for cooling in the case of hot buffer solutions), the tube was closed and shaken by hand to mix the dyes, and the solution was injected for HPLC analysis. The eluent volumes were 5 mL for easily desorbed dyes from silica and 12–15 mL for difficult desorptions from strong cation-exchange sorbents.

HPLC analysis

Dyes were separated by reverse-phase ion-pair chromatography. In this LC method, the mobile phase consists of an aqueous buffer (with an added water-miscible organic solvent such as methanol or acetonitrile) and an added counter-ion of opposite charge to the sample ion. The stationary phase consists of a silica packing with a permanently held (bonded) water-immiscible organic phase. A NOVA-PAK C_{18} column 3.9 mm x 300 mm, particle size 4 µm (from Millipore, Waters Chromatography Division) was dynamically coated with a 5m*M* solution of heptanesulfonic acid (prepared by dilution of PIC B-7 reagent, by Waters) and applied at 25% fraction of isocratic flow in mobile phase.

Other components of mobile phase, flowing at 1 mL/min, were methanol (65%) and 0.1*M* sodium formate buffer (prepared by dissolving an amount of sodium formate corresponding to 0.05*M* solution, adding an equivalent volume of 88% formic acid, and adjusting the pH of the final solution with solid sodium formate to 3.75). The column was housed in a heated compartment maintained at 70°C. It was fed the selected mobile phase by means of a Model 600 Waters solvent delivery system, which also contained a manual injector with a 20 µL injection loop. Eluted compounds were detected and measured by a Model 990 Waters photodiode array detector. During a run, the spectral data of eluted dyes were collected on a hard disk in the range of 500–655 nm, and then peak areas were integrated for each dye at the wavelength near its maximum absorption (i.e., at 588 nm for crystal violet, 620 nm for malachite green, and 650 nm for methylene blue).



2. Chromatogram of a mixture of methylene blue (MeB), malachite green (MG), and crystal violet (CV)

Figure 2 shows a chromatogram of a mixture of these dyes plotted at 588 nm. Peaks are relatively broad and slightly tailing, but this is common in chromatography of ionic compounds. Calibration curves of the dyes were found to be linear up to the concentrations of 100 mg/L;

the measured concentrations were in the range of 0.5–10 mg/L. The concentration of dyes in the eluents collected from SPE columns were obtained by comparing the ratios of the peak areas of injected samples with those of the standards used also for spiking. Recoveries were calculated from the amounts found by HPLC analysis to those used in spiking.

In the initial stages of HPLC analyses, we flushed the entire chromatographic system with a methanol–water mixture before shutdown. This is a required step to prevent the deposition of salts in pumps and in the detector cell. However, this repeated flushing proved to be very damaging to the column that was saturated with ion-pairing reagent. The retention characteristics of the column quickly changed, and a high back pressure developed. Eventually, the column became plugged and had to be discarded. (It was later learned that the manufacturers are aware of this problem, but it has not been described in the literature.) For subsequent analyses, the column was stripped of buffer, disconnected, and stored with ion-pairing reagent following use. Then, with an empty tubing in place of the column, the instrument was flushed with a methanol–water mixture before shutdown.

Chemicals used

Water used for the preparation of buffer and for dilution of ion-pairing reagent was of HPLC purity by Burdick and Jackson (B & J); that used for spiked aqueous solutions was doubly distilled in a glass still. Methanol and acetonitrile, both by B & J, were of HPLC quality. Isopropanol 99.8%, pure GC grade, was from Anachemia.

Formic acid, 88%, was "Baker analyzed" reagent grade. Sodium formate was ACS reagent grade, 99+%, from Aldrich Chemical Co., Inc. Sodium chloride was ACS certified grade from Fisher Scientific Co.

Crystal violet [(C.I. Basic Violet 3), chloride salt, ACS reagent grade] and malachite green [(C.I. Basic Green 4), oxalate salt, certified] were from Aldrich. Methylene blue [(C.I. Basic Blue 9), chloride salt, USP grade] was from Fisher Scientific Co.

Effluent and paper samples

Method development was carried out with effluents from two Canadian newsprint mills. One effluent, which was taken after the secondary treatment system, contained 96 mg/L Na and 16 mg/L K. The other effluent was obtained from the outlet of the primary clarification system and contained 130 mg/L Na and 23 mg/L K.

Two unprinted newsprint samples were used for migration studies: one was made from a thermomechanical pulp (TMP) with sodium hydrosulfite bleaching and the other from a stone groundwood (SGW), also with sodium hydrosulfite bleaching.

Migration tests

Two sets of extractions in a Soxtec apparatus were performed on newsprint samples obtained from two mills using methyl violet. One set was extracted with water and the other with a mixture of 1:19:80 formic acid:water:methanol. In each case, about 3 g of paper (shredded and crumpled) were extracted by boiling in 70 mL of solvent for 2 hours. After extraction, cooled aqueous extracts from four cups were combined into one aliquot, which was then slowly passed through a conditioned silica SEP-PAK cartridge to concentrate the dye. This sorbent was selected with the intention to recover and measure at least a portion of the concentrated dye. Acidic methanol extracts, which were already perceptibly blue, were centrifuged and measured directly by HPLC.

RESULTS AND DISCUSSION

An SPE material that exhibits high efficiencies in concentrating analytes from dilute solutions should have the following characteristics:

- It should quantitatively retain the analytes from large sample volumes.
- Desorption of the preconcentrated analytes must be achieved with small volumes of eluents under conditions that are compatible with the chemistry of the analytes and with subsequent analytical methods.
- Matrix components present in samples should not interfere in the sorption, desorption, and analysis steps.

In this study, several cation-exchange materials and other sorbents were tested to concentrate basic dyes from effluents and water samples.

Concentration of dyes from aqueous solutions

All of the tested cation-exchange materials exhibited high degrees of sorption for dyes in dilute distilled water solutions. These materials included strongly acidic exchangers (cross-linked styrene/divinylbenzene co-polymer with sulfonic acid groups as exchange sites and silica with bonded propylsulfonic groups), exchangers of an "intermediate strength" (cellulosic fibers with phosphate groups or ethylsulfonic groups), and a weakly acidic exchanger (acrylic polymer resin with carboxylic groups). In addition, three other SPE materials (i.e., unmodified silica, silica with diol groups, and silica with C_{18} groups that are not considered ion exchangers) extracted dyes from aqueous solutions. Among them, unmodified silica appeared to produce the best results in the extraction step in terms of an intense narrow band of the three dyes concentrated on the top part of the SPE column.

The literature data indicate that silanol groups are partially ionized at pH 5 *(11)*; a pH value of 7.1 has been reported for silica *(12)* from indirect measurements of acidities of surface hydroxyl groups of various oxides. Thus, silica behaves as a weak cation exchanger with a high capacity in the extraction of dyes from solutions at neutral pH. On the other hand, modified silica supports are likely to sorb the dyes by two mechanisms: those characteristic of the bonded phase (e.g., nonpolar interactions of C_{18} groups) and that due to residual silanol groups (if they are not capped). Our observation that silica with bonded propylamino groups did not concentrate the dyes (as was also the case with basic alumina support) would suggest that the former mechanism predominates. The cation-exchange capacity of octadecyl-bonded silica has been investigated *(13).* From sorption of ferric ions it was found to be in the range of 0.1 to 0.5 μeq/g, which is generally small, but nevertheless a significant fraction (up to about one-third) of the dye loadings in our extraction experiments.

Concentration of dyes from mill effluents

When large volumes (0.5–1.0 L) of effluents, spiked with known amounts of dyes, were passed through various SPE columns, only the strong cation exchangers satisfied the first prerequisite of quantitative extraction from dilute solutions. With other materials, including underivatized silica, breakthroughs of the dyes occurred soon after passing small volumes (approx. 50 mL) of effluent. That is, the dyes were not concentrated into a narrow band (as expected for a good SPE material) but were scattered over the entire column. After large volumes of effluent were passed through the column, the dyes were uniformly distributed through the column. The breakthroughs occurred even when three silica cartridges were connected in series, implying that the dyes could not be completely retained on a length of column that would be useful for practical purposes.

We believe that salts present in effluents are the probable cause of the interferences in the sorption of dyes on weak cation exchangers. From the literature *(14),* we know that ion exchange resins containing carboxylic groups will strongly sorb small ions with large hydrated radii, such as Li^+ and Na^+, whereas the reverse occurs for resins with strong acid groups (i.e., the least-hydrated Cs^+ is preferentially sorbed). However, the position of dye cations relative to the known selectivity orders of alkali cations is not known. To ascertain this position, a sodium chloride solution (1 g/L) in distilled water was spiked with the dye mixture, and then the preconcentration of dyes was tested on silica, sulfoethoxycellulose, and phosphorylated cellulose. The results of the sorption step were similar to those obtained with spiked mill effluents in terms of breakthroughs and poor retention of dyes. Regardless of the exact cause of the poor retention of dyes from salt solutions and from effluents (whether it is high selectivity of the exchangers for Na^+ or effect of high ionic strength), it is evident that these materials are not suitable for the preconcentration of dyes from effluents.

Elution of dyes from strong cation exchangers

To elute bound ions from an ion exchanger, it is necessary to displace them with other competing ions that are preferentially sorbed onto the exchanger or are present in large amounts in the form of high concentrations or large volumes of eluents. One of the strong cation exchangers tested for dye sorption, styrene/divinylbenzene resin with sulfonic acid groups, bound the dyes so strongly that the extracted dyes did not appear as an intense violet-blue band, but turned pale green on contact with the resin. With such strong bonds, it is possible that the dyestuff cations were converted into their nonchromic forms. The strong binding impeded elution, even with a mixture of concentrated hydrochloric acid and potassium chloride, which, in any case, would not be suitable for the subsequent determination of dyes by any method based on their spectral properties. It is known that in very acidic solutions, triphenylmethane dyes are transformed into weakly colored protonated (i.e., doubly charged) cations *(3).* This is the basis for their application as acid–base indicators *(15)* in low pH ranges (e.g., crystal violet is used for titrations with endpoints of pH 1.8 or less).

In the case of silica with bonded propylsulfonic acid groups, the dyes were strongly retained in a narrow band, but their colors did not change on sorption. To elute them, a number of mixtures were investigated, including hot concentrated buffer solutions mixed with organic solvents, salt solutions of aromatic bases (aniline hydrochloride, pyridine hydrochloride, and p-phenylenediamine dihydrochloride) in water and in methanol, and saturated aqueous solutions of calcium lactate and barium acetate. (The latter group of eluents was tested only for a comparison of the affinity of the dye cations for the exchanger with that of Ca^{2+} or Ba^{2+}; these eluents would not be compatible with the HPLC analysis method.)

All eluents were applied in the "backflush" mode (i.e., the SPE cartridge was turned upside down to reverse the flow), since the sorbed dyes formed a narrow band on the top of the column. None of the solutions tested led to the complete elution of dyes from the sorbent. After initial elution with 1–3 mL of elu-

Dye	Percent recovery with (A)*	Percent recovery with (B)**
Crystal violet	60	64
Malachite green	50	87
Methylene blue	57	82

*(A) 10% (v/v) of 0.4*M* sodium formate buffer in acetonitrile
**(B) 50% (v/v) of 2*M* sodium formate buffer in isopropanol

I. Recovery of dyes from a silica-based strong cation-exchange sorbent eluted with 15 mL of hot buffers in organic solvents

Amount of dye loaded onto SPE column, µg	PERCENT RECOVERY OF DYE		
	Crystal violet	Malachite green	Methylene blue
10	92	94	98
40	98	98	100

II. Recovery of dyes from a silica sorbent eluted with 5 mL solution of 1% formic acid in methanol-water mixture

ents, an intensely colored front appeared in the collected solution. However, some dyes remained on the column, even after elution with much larger volumes than practical (10–15 mL). From among the eluents tested, hot buffer solutions mixed with an organic solvent were the most efficient. Sodium formate buffer was selected, because its low pH value (3.75) is above the pH at which the dyes transform into protonated dyestuff cations, and because it was compatible with the mobile phase and column used in HPLC measurements.

Table I shows recoveries of dyes, obtained from duplicate experiments, from Supelclean LC-SCX extraction tubes after elution with two different buffers. The dyes were sorbed from 0.5 L portions of effluent spiked with 0.04 mg/L each of the dyes. It should be noted that the sorption and elution steps are independent. The low recoveries are due to incomplete displacement of the dyes from the columns. Indeed, the dyes were still visible on the columns after elution. With a 2*M* buffer solution, the recoveries were higher. Unfortunately, this eluent was not suitable for repeated HPLC analyses, because injections of such solution (high ionic strength) caused a noisy instrument baseline for several hours.

Strong interactions between some organic ions and ion-exchange resins have already been described in the literature, and they are attributed to the sum of coulombic and van der Waals forces. Quarternary ammonium cations containing aromatic structures, e.g., benzylammonium, were found to be particularly strongly sorbed on sulfonated polystyrene resins *(14, 16)*. Irreversible sorption of a long-chain aliphatic cation (trimethyloctadecylammonium) on a commercial strong cation exchanger (type not specified) was also reported *(17)*.

KEYWORDS
Basic dyes, cation exchangers, cationic compounds, chemical analysis, chromatography, dyes, effluents, extraction, ion exchangers, liquid chromatography, measurement, newsprint, printing papers, sample preparation, separation, separators, sorbents, test methods, wastes.

Elution of dyes from weak cation exchangers

Dilute solutions of formic acid in water–methanol mixtures eluted the dyes from all the weakly acidic materials tested. **Table II** shows the recoveries obtained from duplicate runs of dyes that were sorbed from 2 L aliquots of aqueous solutions (spiked at 0.005 and 0.02 mg/L with each dye) and then eluted (reverse flow) with 5 mL portions of a mixture of 1% formic acid, 19% water, and 80% methanol. The high recoveries of dyes from silica with this eluent are not surprising. The retention behavior of various cations on silica columns used in HPLC indicates that silanol groups are slightly dissociated at pH > 4.5 *(11)*. At pH values less than 4, silica is considered neutral or may be positively charged *(11)*. If this would occur during elution of the dyes with an acidified solvent, the result would be a more effective displacement of the dyes than elution with competing cations from strong exchangers.

Note again that silica is not a good SPE sorbent for concentrating dyes from large volumes of effluents. For example, recoveries obtained after spiking an effluent containing 130 mg/L sodium were only 34%, 17%, and 9%, respectively, for crystal violet, malachite green, and methylene blue on elution with a 1% formic acid solution. The major portions of the dyes were not retained on the sorbent, as observed by the breakthrough of colored front during extraction.

Estimation of dyes in newsprint effluents

Since the silica-based strong cation-exchange sorbent was found to extract dyes quantitatively, without a change in their intense color, it is possible to use this property to perform a semiquantitative test for the

dyes. The color intensity of the sorbed dye is proportional to the sorbed amount. By comparing the dye intensity recovered from a sample with that produced by a standard amount, one can obtain a rough estimate of the dye content of the sample. The test could be performed easily in mills, since it does not require any sophisticated instrument. Using this approach, as little as 0.02 mg/L of dye can be detected.

Mill effluents tend to have a brown color, which masks the presence of dyes at low concentrations. However, these colored compounds do not interfere with the extraction of dyes, since they are not concentrated on the sorbent.

The presence of dyes in an effluent was tested visually on a set of three 0.5 L aliquots, two of which were spiked with the dye mixture at 0.02 and 0.04 mg/L concentrations of each dye. When the three aliquots were passed through three prewashed LC-SCX tubes, an accumulation of a narrow band of dyes was observed at the top of the sorbent bed after passing only 70 mL of the effluent spiked at 0.02 mg/L. No dye coloration was observed on the unspiked sample, even after elution of the whole sample. This implies that, if any dye compounds were present in the effluent, their concentrations would be less than 0.02 mg/L. At the end of the extraction of the two spiked aliquots, the amount of dyes loaded on the cartridge seemed to be greater from the more concentrated sample.

We suggest a similar procedure for the testing of dyes in effluents. As a first step, suspended solids should be removed from the effluent by sedimentation, and a fairly large aliquot (e.g., 0.5 L) should be passed through the sorbent. Then, if any dye band appears on the column, two series of spiked standards prepared with effluent and with water (e.g., at concentrations of 0.02 and 0.04 mg/L) should be extracted to compare the band intensity on cartridges. Such a method can detect only the dissolved dyes in effluents and not those sorbed on suspended solids. The latter are considered to be relatively inactive as toxicants. Dissolved dyes would likely be present in effluents only during occasional spills or dumpings of stock dye formulation.

Migration of dyes from newsprint

No visible coloration was observed on the SPE column after concentration of aqueous extracts. Nevertheless, the column was eluted with acidic methanol mixture, and the eluate was measured. No chromatographic peak was measured. Since the HPLC detection limit of the dye in the concentrated eluate was about 0.05 mg/L (based on twice the signal-to-noise ratio on the chromatogram), the complete extraction procedure would detect 0.02 µg/g of dye migrated from paper if a 100% SPE efficiency could be assumed. A more conservative estimate of limit of detection, assuming only 10% SPE efficiency, is 0.2 µg/g.

The results in **Table III** show that acidic methanol, unlike water, was a good solvent for the dyes. Indeed, the paper samples attained a yellowish hue after extraction with the solvent. In contrast, samples extracted with hot water retained their grayish tint.

Sample	AMOUNT EXTRACTED, µg/g, (on weight of the paper) With hot water	With hot acidic methanol
Mill A	<0.2	10
Mill B	<0.2	24

III. Solvent extraction of methyl violet from newsprint samples

CONCLUSIONS

Among the various types of SPE materials tested, only strong cation exchangers completely retained newsprint dyes from spiked effluents. The incomplete retention on other materials is attributed to interfering components (salts) present in effluents.

A resin with an aromatic network structure and sulfonic acid groups as exchange sites held dyes more strongly than a silica-based support with propylsulfonic acid groups. This suggests that there is a large contribution from π-electrons to the force of attraction between the resin and dyes.

A good eluent for quantitative desorption of dyes from strong cation exchangers was not found. Consequently, a semiquantitative test is proposed using a silica-based strong cation-exchange sorbent. With this technique, the presence of dyes in effluents in the 0.0 -mg/L range can be detected visually provided large effluent volumes (approx. 0.5L) are used.

For the concentration of dyes from highly diluted distilled water solutions, underivatized silica is an excellent material. Their complete elution is achieved with small volumes of 1% formic acid in aqueous methanol.

The dyes used in newsprint manufacture are so strongly attached to fibers that they cannot be extracted with hot water. **TJ**

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