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Chromatographic Examination of Intaglio Inks, Resins and Varnishes

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Executive Summary

More than eight hundred chromatograms were taken of over one hundred and thirty BEP inks using five means of detection. While hardware problems forced some of the samples to be rerun, there were enough successful runs to investigate correlations of the resultant chromatograms with BEP measured crumple and laundry results.

Old and new formulations of black and green cylinder wipe currency inks, gave different chromatographic results. GPC should be able to distinguish different formulations if the differences are as large as was true for the ones supplied.

Extracts from the retain samples supplied by the ink manufacturer have a high correlation to extracts from the same ink batches taken from the drums. It seems likely that there will be no need to obtain ink samples from the drums for testing; samples of retains would be adequate for the testing. Chromatography could therefore be done on representative samples before a drum is used for printing.

Different batches of the same ink formulation can have a large variation on GPC results, demonstrating that batch-to-batch variations exist. Match factors have been calculated for a series of black and green cylinder wipe currency inks, and average chromatograms of many inks of the same type. A correlation may exist between extracts with low match factors and inks with low crumple numbers. A scarcity of samples with low crumple numbers hampers the determination of the exact nature of the correlation. No correlations of chromatographic results with laundry numbers were found, but no samples were tested that had poor laundry results.

To properly correlate the BEP measured properties with chromatographic results, many samples with a wide range of properties must be collected. It is proposed that retain samples are set aside each time poor results in BEP tests are found. These, along with a number of inks giving good results would provide a statistically significant sampling.

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1: Introduction

Quality assurance tests on incoming intaglio inks used in the printing of currency are limited to measurements such as rheology and volatile organic content. The most revealing tests, crumple and laundry resistance tests, are carried out only after full press runs. These tests determine whether a whole batch of currency is acceptable or not. A screening test is desirable to find unacceptable ink batches before the printing has begun. Such batches might be set aside and reformulated into acceptable inks.

Intaglio inks are complex mixtures of many components such as polymerizable compounds, solvents, surfactants, driers, pigments, fillers, etc. The components effect the final properties of the printed currency in various ways. Gel permeation chromatography (GPC) can be used to characterize the molecular size of the large, polymeric components present in the ink. Since these compounds are responsible for the crosslinking that takes place in the air drying process, variations in their chemical composition and molecular size are expected to have important effects on the properties of the printed currency.

It has been demonstrated [1] that the soluble components of intaglio cylinder wipe currency inks can be distinguished by GPC. Two samples that are supposed to be the same, actually are not because they exhibit quite different chromatograms. When the inks are used in printing the resulting currency can have very different durabilities. A much larger body of data is necessary to correlate features of these chromatograms with durability of the printed matter.

2: Background

2.1: BEP Requirements

Currency inks are made in batches and are shipped in two drum lots. Each batch is made to the same specifications, but some batch to batch variations must exist. A small sample of each batch known as a "retain" is sent to BEP for testing. If the retain samples are truly representative of the material in the drums, then the incoming inks could be easily studied by GPC through use of the retains. If the contents of the retain container have changed in some way, then the samples would have to be taken from the drums for the GPC work. The added effort required to gather the samples would probably make routine analysis of the inks impractical.

This technique is not an attempt to identify the contents of an ink, but rather it is an empirical method of monitoring the size distribution of compounds extracted from the inks using solvents. Differences in the chromatograms prove that different batches are not exactly alike, but unless some features of the chromatograms can be correlated to important properties such as durability, the differences in the GPC chromatograms will not result in a useful screening process.

If a correlation is found between GPC results and unacceptable ink batches, the drums can be set aside. Due to the empirical nature of the results, it is unlikely that batches could be rejected and returned. Rather, attempts could be made to reformulate suspect batches into acceptable inks by addition of appropriate ingredients. A procedure similar to this is already in place to reconstitute inks recovered in the printing process.

2.2: Gel Permeation Chromatography

Gel permeation chromatography separates soluble compounds by molecular size. The chromatographic column is packed with a porous material (gel) that contains cavities with sizes in the same range as the hydrodynamic volume of the molecules studied [2]. This ranges from 10 nm to 1000 nm for most polymeric molecules. As the molecules in the carrier solvent move through the column they diffuse into the pores, and while in the pores, remain stationary while the carrier solvent flows past. This causes the molecules to elute later than if they had not entered the pores. The larger the molecule the fewer the pores it can enter and the less its flow through the column is retarded. Therefore large molecules elute faster from the column than do the smaller ones.

The hydrodynamic volume of a polymer is the parameter that controls when it appears in the eluted volume. The relationship between hydrodynamic volume and molecular weight depends on the polymer and solvent type and on such polymer structure as branching content. The exact nature of the polymeric material in the inks is unknown but probably includes complex branching. Therefore it is not possible to express the distribution of molecular sizes in the ink extract in terms of molecular weight. Whenever ink extracts are run, polymer standards are also run. The standards are polystyrenes with narrow molecular weight distributions with molecular weights from a few hundred to a few million daltons. The calibrant used most often in this work was a commercial sample made by Polymer Laboratories known as Easical [3]. It is a mixture of polystyrenes with molecular weights of 3,040,000; 333,000; 66,000; 9,200; and 580 daltons. This information can be used to express the size distributions of the ink extracts in terms of hydrodynamic volume.

2.3: Detectors Used

After the polymeric components of the ink extracted by solvent have passed through the columns, they flow through a series of detectors. The response of the detector depends on the amount of the material and the physical characteristics of the material. Since it appears that ink extracts are mixtures of components with different physical characteristics [2], the response from a detector is typically not proportional to concentration of a single material, but is a composite response from all materials. It has been shown previously [1] that UV absorption at different fixed wavelengths give different shaped chromatograms.

A Spectra Physics Spectra Focus [3] detector was used, with 230, 240, 254, and 275 nm wavelengths being monitored. Each response was compared with average responses compiled from many extracts. For the runs listed in Table II with a + in the column at the far right, a second single wavelength detector set at 254 nm was used to check the stability of the multiple wavelength detector.

A mass evaporative detector (MED) was used in all runs. The run stream is nebulized, and the solvent in the dispersed droplets is evaporated. The nonvolatile high molecular weight components remain behind and a beam of light is scattered from the resultant particles. The response from such a detector is a non linear function of concentration in most cases. Theory predicts [4] that the response goes as the square of the concentration in the limit of extreme dilution and follows the power law $C \alpha R^a$ where the concentration, C, is proportional to the detector response, R, raised to a power a. Polystyrene calibrants were found to have a value of the power equal to 0.53 in this concentration range [5]. This number was used to convert the detector response to concentration for the ink extracts also. Since the MED results were not as useful in correlating the properties of the printed inks, no attempt was made to calibrate the MED for the ink extracts.

2.4: Review of Previous Results

Work done for BEP in FY90 proved that GPC is a useful technique for distinguishing inks. Different ink types such as heat set, air dry paperwipe, air dry water wipe, and reconstituted inks, yield very different chromatograms. Thus, different ink classes can easily be distinguished.

Two inks that were nominally the same ink type and formulation were run repeatedly. Currency printed with these inks was tested at BEP and found to have extremely different durability as measured by crumple numbers. Chromatography of these two ink extracts in tetrahydrofuran (THF) containing the stabilizer butylated hydroxy toluene (BHT) easily identified each sample. It could not be determined whether these differences correlated with the crumple results, but it was obvious from the GPC results that batch-to-batch variations in the resin existed.

The objective of the work done in FY91 was to run more samples with a range of crumple and laundry numbers to see if correlations existed with the chromatograms. The method used was to run many ink extracts from different ink samples, all manufactured according the same formulation. For each detector's response, an average of all of the ink extracts was made. Match factors [1] were calculated between each ink and the average of all inks. Correlations were then checked between the match factors and the crumple and laundry numbers supplied by BEP.

3: Gel Permeation Chromatography of BEP Inks

3.1: Instrumental Problems and Changes

3.1.1: Mass Evaporative Detector Upgrade

Previous work done with ink extracts proved that 254 nm UV detection was better than MED detection. An important factor was the lack of sensitivity of the MED. In the Summer of 1991 the MED was returned to the manufacturer for hardware modifications that greatly increased the sensitivity. Figure 1 shows the MED response of an ink extract before and after this change. Before the upgrade the response was very low, resulting in the jagged line shown in figure 1. The smooth line is the response of the upgraded detector. Outputs containing erratic, noisy signals will give poor match factors even if the samples are identical.

3.1.2: Stability of Flow Rates

Shortly after the beginning of this work, the polystyrene marker peak began to shift in elution time. This is often an indication of leaks in the flow system, or leaks in the valves of the pump. The pump was disassembled and components were replaced several times. Temporary improvements were sometimes achieved, but the problem seemed to reoccur after a short period. A new pump manufactured by Isco [3] was installed. It proved to give a much more stable response, going for long periods of time with reproducible marker peak positions.

Clearly, marker peaks must be used in work of this nature. Some slight movement of the chromatograph peaks with time is unavoidable. In that case, the use of marker peaks allows for an internal set of standards to calibrate each chromatogram. Figure 2 shows 254 nm UV response of inks run on three separate days. In figure 2a the raw data is shown. The sharp peak to the left is the polystyrene marker peak and should appear at the same place each time if there are no flow rate problems. The sharp peak to the right is the stabilizer, BHT, in each case. Figure 2b is a plot of the same data shifted so that the two marker peaks coincide. The plots are now much more uniform. The slight differences in the chromatograms in the middle are the variations in batch-to- batch formulations that are sought.

The chromatograms were broken into 500 data points by interpolation of the original data. Match factors were calculated for the points numbered 80 to 421 when THF was the extraction solvent and between 40 and 370 when methyl ethyl ketone (MEK) was the extraction solvent. This eliminates any data that were influenced by the polystyrene marker or low molecular weight material such as BHT. In the case of the MEK extracts, MEK itself was used as a marker instead of BHT.

3.1.3: Changes in the Columns and Inks

Other problems of reproducability occurred throughout this work. Figure 3 demonstrates a baseline instability that occurred quite often. To the left of the sharp polystyrene marker peak, the baseline should be flat with no material eluting. Many attempts were made to improve the stability. An additional UV detector also recorded the baseline drift, proving that it was not a detector problem. There are several possible sources of this variation. It is known that polar material, which is probably present in the ink extracts, can cause problems in polystyrene-divinyl benzene GPC column fillings [2,6]. Absorption of the polar compounds extracted from inks onto the chromatographic column can cause it to act similar to a liquid chromatography column. Retention of the polar compounds can be delayed, and they may actually elute during the next run. The best performance was obtained when a column was new or when it had been flushed with solvent for an extended time. While the exact cause of this problem is unproven, it seems necessary to study it in detail. It may be necessary to flush a column periodically to renew its original condition.

The work done in FY90 used THF stabilized with BHT for both the extraction and the flow stream. At the beginning of this year's work, a switch was made to unstabilized THF in an effort to improve the UV detectors response. It was noticed that over periods of several hours, slight changes in chromatograms resulted. Figure 4 is a plot of five sequential chromatographic runs from the same vial of an unstabilized ink extract. Over a period of several hours the region in the high molecular weight region of the chromatograms increases regularly. It appears that the extract is changing during the period of time required for the chromatography. This would lead to match factors that would change with time. Shortly afterwards, we reverted to THF stabilized with BHT for the extraction and the solvent flow. The 230 nm UV response was severely degraded because of the UV absorption of BHT present in the GPC solvent but the procedure appeared necessary to prevent changes in the extract.

Another puzzling feature appearing in some chromatograms is shown in figure 5. A sharp peak eluted before the one million molecular weight polystyrene marker peak. In another run this feature elutes before a polystyrene of ten million molecular weight. It is possible that it is ink extract that has begun to gel, but it occurred even in THF containing larger levels of BHT than previous runs that did not have this feature. The last GPCs taken used MEK as an extraction solvent. MEK does not form peroxides as THF does and may allow for longer stability. The runs made with this extraction solvent did not show the anomalous peak at the beginning of the chromatograms.

There are many unanswered questions about the irreproducibility of the chromatography that must be answered before GPC can be used to reliably screen incoming inks. Different columns, column conditioning, or solvents may be necessary to achieve this. In spite of these problems, there were sufficient runs without anomalies to allow us to test for correlations between GPC results and BEP durability tests.

3.2: Comparisons of Ink Extracts

3.2.1: Description of BEP Inks and Chromatograms

Table I presents a list of the BEP printing inks used in this study. Each ink was given a NIST identification number ranging from 1 to 139. The BEP identification numbers are also listed along with each formulation number, color and ink type.

Upon request of BEP personnel, a few paperwipe and postage inks were run at the start of the project and the resulting chromatograms were delivered to them. The chromatograms closely resembled those shown in the annual report for FY90 [1]. Since these inks have no correlation with conventional cylinder wipe currency inks, they will not be discussed here.

A large majority of the inks listed in Table I were from two current formulations. Over one hundred samples of present black, cylinder wipe ink (designated 374017K) and the present green cylinder wipe ink (designated 354033A) were run. Two other similar ink formulations were also run. An old formulation of the black ink (designated 374017A) and an old formulation of the green ink which was replaced only very recently (designated 354100J) were studied to determine if GPC was capable of detecting formulation changes.

Table I also lists crumple numbers and laundry numbers for many of these inks, as measured by BEP. These were the primary parameters to be correlated with the chromatograms. Both crumple and laundry numbers range from 6 to 0, with 6 being the best.

Table II lists the GPC chromatograms taken of the extracts of the inks listed in Table I plus chromatograms of polymer standards and blanks. More than 800 chromatograms were taken under a variety of chromatographic conditions. The first column in Table II, SEC #, is a unique identification number that is assigned to each chromatographic run by the GPC software. The column labelled "Sample" refers to the NIST ID number that was assigned in Table I. The seven columns to the right in the table identify the major chromatographic changes that took place during this project. The "BHT/flow" column indicates when BHT stabilizer was in the solvent (THF) flowing in the column. The "BHT/ext" column gives the extraction solvent, a - being THF without BHT, a + being THF with BHT, and MEK being methyl ethyl ketone. "Rerun of old samp" indicates that a previously prepared, old sample was run to judge aging effects. The "Isco" column has a + when the original solvent pump was replaced with the ISCO solvent pump [3]. Similarly, a + in the "MED upg" column shows when the upgraded mass evaporative detector was used. The "2nd UV" column has a + to indicate when an additional 254nm UV detector was used to check the original detector.

3.2.2: Differences in Green and Black Formulations

Figure 6 is a plot of the 254 nm UV detector response of four ink formulations. The solid line is the current black ink, 374017K; the short dashes are an old black ink formulation, 374100J; the dots are the current green formulation, 354033A; and the long dashes are an old green formulation 374017A. In all cases the narrow peak to the left of the chromatogram is the polystyrene marker. The same weight of ink was subjected to solvent extraction with the same volume of solvent in each case.

All four of the chromatograms have very different features. The old black formulation has a weak peak at 22 mL compared to the others. This represents the higher molecular weight components of the ink. Since this ink was more than two years old, it is possible that the original high MW components have crosslinked, and were not extracted by the solvent, or that perhaps the original formulation was different. The old green ink had a large amount of material eluting at 22 mL. The new green formulation appears to be more similar to the new black formula than to the old green formulation.

The differences between formulations of an ink appear to be large enough to easily distinguish among the inks. These variations seem to be greater than the batch to batch variations of a given ink formulation. It is likely that GPC can determine the formulation of an incoming ink.

3.2.3: Comparisons of Press and Retain Inks

The most practical way of testing incoming batches of ink is to test the contents of the retain samples that are sent with each batch of ink delivered. In this way the drums never need to be opened before the actual printing operation. For this to be successful, the contents of the retain containers need to be very similar to the drum contents. If significant differences exist between these two samples, any testing of retain samples, including those currently being done at BEP, may not be truly representative of the ink that is actually used in printing currency.

Eleven pairs of black retain and press samples were supplied to NIST by BEP personnel. The eleven pairs were examined under two chromatographic conditions, THF with BHT as the extraction solvent with unstabilized THF as the flow solvent, and MEK as the extraction solvent with stabilized THF as the flow solvent. Figure 7 shows the 254 nm UV detector response for three ink pairs under the first chromatographic conditions. The pairs of solid lines, long dashes, and short dashes are for retain and press samples of the same ink batches. Ink extracts from the two sources give chromatograms that are very similar, with differences between two ink batches being much greater than between two sources of the same ink batch.

Match factors were calculated for all combinations of chromatograms for both the THF extracts and the MEK extracts. Four averages were taken for the match factors from each of the five detectors. Figure 8 is a plot of these averages for each detector. The triangles are average match factors for all retain-press ink pairs extracted with THF. The square symbols are average match factors for all combinations of THF extracts. The diamond symbols and circles are for retain-press pairs and all combinations of MEK extracts, respectively.

In every case, there is a higher average match factor for retain-press pairs than for other combinations, for any set of chromatographic conditions. For the mass evaporative detector, the differences are not great. The greatest differences in the responses occur for the larger molecular components (those to the left in a chromatogram). The MED does not give a strong signal at the concentration present in this range and hence there are smaller differences. Similarly, 270 nm UV is not sensitive to these components, and the match factors are not well separated. Although the MEK extracts show poor match factors in all cases at 230 nm, this is not due to the MEK. The MEK extracts were eluted from the column with THF containing BHT which has strong absorption at 230 nm. This makes the signal weak and noisy. If stabilized THF needs to be used in the flowing solvent to prevent changes in the ink extract, then 230 nm will not be a useful wavelength to use.

The best results for both THF and MEK extracts were found using the chromatographic responses measured at 254 nm. The retain-press pairs have match factors near 1000 indicating that they are very similar, while random combinations show considerable differences. **It appears that these retain samples are very representative of the contents of the drums. Testing of retain samples should give results that accurately describe the printed ink, and therefore there is no need to collect samples at the time of printing.**

While match factors of various inks can provide important information on the batch to batch uniformity, match factors of any ink extracts obtained using different solvents will be poor. Figure 9a shows chromatograms of a retain-press pair (NIST #67 and 68) extracted into THF (solid line) and MEK (dashed line). The elution volume scale is usually established by matching the peaks due to the polystyrene marker at low elution volume and the BHT stabilizer at high elution volume. When MEK is the solvent, the strong absorption of MEK at 254 nm interferes with detecting the BHT. Therefore, the curves in Figure 9a were scaled so that the MEK signal at high elution volume was matched to that from the BHT in the THF solvent. Chromatograms from a given retain-press pair are similar in a particular extracting solvent but there are large differences for the same ink extracted with different solvents. If one uses the strongest peak from each ink extract to establish the elution volume scale at high elution volume, as shown in Figure 9b, peaks generally occur at similar elution volumes, but the intensities from the two solvents are different and match factors are correspondingly low. Therefore it is not possible to build up a data base unless a single extracting solvent is chosen.

3.3: Correlations Between BEP Tests and GPC

3.3.1: Correlation Between Crumple and Laundry Numbers^

Table I lists results of BEP tests for crumple and laundry numbers for many black and green inks. It is of interest to check for a correlation between these two parameters. If both properties are dependent on the same characteristic of a particular ink, there should be a strong correlation between these two properties. Figure 10 contains plots of crumple number versus laundry numbers. Figure 10a contains data for black inks and 10b for green inks. There is no obvious pattern displayed, and the two properties seem uncorrelated.

More definite conclusions cannot be drawn due to a lack of a wide range of data. For black inks, only one sample has an exceptionally low crumple number, 2.8, and only three are between 4.0 and 5.0. The laundry numbers range from 4.0 to 5.6, and none is exceptionally low. There is even less of a range of values for the green inks. All crumple numbers are greater than 5.4 and all laundry numbers are greater than 4.9. There is little chance of finding any correlations in the green inks because of this. The black inks have a wide enough range for study of correlations with the crumple numbers, but due to the scarcity of samples with low numbers, the statistics will be poor.

If there is no correlation between crumple number and laundry number, then any single feature of the chromatography could at best be correlated to only one of these numbers. It is possible that different areas of a chromatogram or different detector responses may have correlations with crumple and laundry. To check this, match factors of all of the detectors were examined.

3.3.2: Comparisons of Detectors for Black Inks

The chromatograms were characterized by first averaging each detector response for all inks of a given class: black inks extracted with THF, black inks extracted with MEK, and green inks extracted with MEK. Each individual ink extract was then rated by measuring the deviation of its chromatogram from the average. The method used was the "match factor" method as was previously described [1]. It is a least squares type of fit that is sensitive to the shape of the chromatogram. A value of 1000 is a perfect match and lower values represent increasingly poorer fits.

Figures 11 through 15 plot crumple numbers and laundry numbers versus match factors calculated from chromatograms obtained by using the mass evaporative detector and 230 nm UV, 240 nm UV, 254 nm UV, and 270 nm UV wavelength. All of the inks were the current black formulation and extractions were made with THF stabilized with BHT. The chromatography was performed with unstabilized THF as the flow solvent.

Figure 11 plots the crumple and laundry results against the match factors from the mass evaporative detector. The lines in Figure 11 are least squares fits to the points. The points are spread out with no real correlation. Figure 12 is a similar plot for match factors calculated from the 230 nm UV detector. In figure 12a the points still have some scatter, but a correlation seems to be present between the crumple number and the match factor. The inks that differ the most from the average tend to have lower crumple numbers. The laundry numbers have poor correlation.

The match factors from the 240 nm UV detector (Figure 13) exhibit correlations similar to those of the 230 nm UV detector. The most strongly correlated results are for the match factor from the 254 nm UV detector and the crumple numbers as seen in figure 14. Figure 15 shows that at 270 nm, the correlations are absent.

While it is necessary to test a larger number of samples with a greater range of crumple numbers to insure a reliable data base, the results shown in figure 14a are very promising. No correlations can be made with the laundry numbers, but the range of test results was a very narrow range. If many more samples with a wide range of laundry numbers could be tested, a correlation could possibly be found with the response of one of the detectors.

3.3.3: Comparisons of Extraction Solvents for Black Inks

Near the end of the present study, several inks were rerun with MEK as an extraction solvent. It proved to be a good solvent for the ink components, extracting a large quantity of material. THF is known to form peroxides which could decompose by reacting with metal driers in the ink and subsequently alter the resin component of the ink. Such changes would change the molecular size distribution of the ink extracts and would introduce errors in the data analysis. MEK has no tendency to form such peroxides and may be a more desirable extraction solvent. The few samples that were run with MEK as an extraction solvent had flat baselines and no sign of buildup of higher molecular weight components.

Figures 16 through 20 are analogous to figures 11 through 15 except that MEK was used for the extraction instead of THF. The only other major change was that THF containing the stabilizer BHT was used as the flow solvent, since by the time the MEK extracts were done, we had become convinced that unstabilized THF in the flow could cause problems. Figure 16 shows the match factors as calculated from the mass evaporative detector plotted against crumple and laundry numbers. As was seen in figure 11, there is no strong correlation of the detector with either crumple or laundry numbers. Figure 17 shows the results for the 230 nm UV detector. The correlations are poorer than shown in figure 12, the 230 nm UV results for THF extracts. This is due to the differences in the flow solvent in the two cases. The MEK extracts were run in THF stabilized with BHT. This has significant absorbance at 230 nm, making the resulting signal noisy.

Figures 18 and 19 are for 240 nm and 254 nm respectively. The correlations here are strong for the crumple number, as was the case with the THF extracts. Figure 20 shows the results for the 270 nm detector, and as with the THF extracts, the correlations are poor. In all cases there are no strong correlations of the laundry number with match factors.

The correlations of match factors with crumple numbers seem to be the best when a 254 nm UV detector is used. Many more inks need to be studied representing a wide range of crumple numbers to accurately determine the relationship, but there seems to be real relationship between the size distribution of ink components and the crumple resistance of the printed currency.

3.3.4: Comparisons of Green Inks

A series of green inks of the current formulation were also tested. They were run in the same manner as the black inks extracted with MEK, as described in the previous section. Figures 21 through 25 plot crumple numbers and laundry numbers versus match factors calculated from chromatograms obtained using the mass evaporative detector and 230 nm UV, 240 nm UV, 254 nm UV, and 270 nm UV wavelengths. No correlations seem to be present in these data. As was shown previously in figure 10b, there is simply not a wide enough range of crumple and range of laundry numbers to develop any correlations. All of the inks are virtually the same.

4: Conclusions

Gel permeation chromatography is prone to a variety of hardware problems that effect the results significantly enough to render it impossible to analyze inks from time to time. Replacement pumps, columns, detectors, etc may be necessary to insure continuous operation. More study is necessary of the basic extraction and chromatographic conditions to identify and eliminate any problem areas.

When the chromatographic conditions are optimum, GPC can easily measure batch-to-batch variations in production inks. Changes in the extractible ink components from ink type to ink type and formulation to formulation are significant enough for easy detection. A well maintained GPC would be an important tool in tracking changes when new formulations are introduced.

The retain samples are good representative samples of the materials in the drums. It is unlikely that taking samples from the press during printing would be necessary in any chromatographic quality assurance operation. Similarly, any other tests done at BEP in a timely fashion on the retain samples probably give results closely correlated to those of the drum material.

While there seems to be a correlation between chromatographic results of black inks and crumple numbers, the lack of a large number of ink samples with a wide range of crumple numbers reduces the degree of confidence in such a correlation. Figures 14 and 19 show that 254 nm UV detection yields the most sensitivity. Match factors from green inks show no correlations with crumple or laundry, but the lack of a wide range of crumple and laundry results makes such correlations virtually impossible.

It is recommended that investigations in this area be continued. Gel permeation chromatography can be an extremely sensitive method of detecting differences in the resin base of ink formulations. However, before it can be used on a routine basis, the solvent and column packing must be optimized and techniques for stabilizing the resin in solution and on the column must be developed. Once these variables are optimized, additional ink samples should be tested. Retain samples from inks which exhibit poor crumple or laundry resistance should be set aside for such a study because these are of greatest interest. A wide range of such numbers is essential to the success of such a study.

References

1. B. J. Bauer, B. Dickens, W. B. Blair; "Chromatographic Examination of Intaglio Inks, Resins and Varnishes", Annual Report FY90, September 30, 1990.

2. for example see J. V. Dawkins, "Size Exclusion Chromatography" in Comprehensive Polymer Science, Colin Booth and Colin Price Eds., Pergamon Press, New York, Volume 1, pages 231-256, 1989.

3. Certain equipment, instrument, or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.

4. M. Augenstein and M. Stickler, Makromol, Chem., 191, 415-428, 1990.

5. B. J. Bauer, unpublished results.

6. Howard C. Jordi, personal communications.

Captions of Figures

1. Normalized MED detector response vs. elution volume (mL) for a black cylinder wipe currency ink extract; jagged line, before upgrade; smooth line, after upgrade.

2. 254 nm UV detector response versus elution volume for three black cylinder wipe currency ink extracts; figure a, unshifted results; figure b, shifted so that polystyrene marker and BHT beaks coincide.

3. 254 nm UV detector response versus elution volume for six black cylinder wipe currency ink extracts; demonstration of unstable baseline.

4. 254 nm UV detector response versus elution volume for a black cylinder wipe currency ink extract injected four times; demonstration of ink extract aging in unstabilized THF.

5. Detector response vs. elution volume for a black cylinder wipe currency ink extract; solid line, 254 nm UV; dashed line, MED; demonstration of occurrence of anomalous early peak.

6. 254 nm UV detector response for four cylinder wipe currency inks; solid line, current black formula 374017K; short dashes, old black formulation 374100J; dots, current green formulation 354033A; long dashes, old green formulation 374017A.

7. 254 nm UV detector response versus elution volume for six black cylinder wipe currency ink extracts; the three pairs of identical are for three different Press-Retain samples.

8. Average match factors between retain-press pairs and all combinations of different black cylinder wipe ink extracts; triangles, retain-press pairs extracted in THF; squares, all combinations extracted in THF; diamonds, retain-press pairs extracted in MEK; circles, all combinations extracted in MEK.

9. 254 nm UV detector response vs. elution volume for cylinder wipe currency ink 67 and 68 extracts; solid lines, THF extracts, dashed lines, MEK extracts; figure a, elution volumes matched at polystyrene marker and matched at BHT/MEK peaks; figure b elution volumes matched at polystyrene marker and matched at main extract peak.

10. Laundry numbers versus crumple numbers for cylinder wipe currency inks; figure a, black inks; figure b, green inks.

11. Crumple or Laundry numbers vs. MED match factors for THF extracts of black cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

12. Crumple or Laundry numbers vs. 230 nm UV match factors for THF extracts of black cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

13. Crumple or Laundry numbers vs. 240 nm UV match factors for THF extracts of black cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

14. Crumple or Laundry numbers vs. 254 nm UV match factors for THF extracts of black cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

15. Crumple or Laundry numbers vs. 275 nm UV match factors for THF extracts of black cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

16. Crumple or Laundry numbers vs. MED match factors for MEK extracts of black cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

17. Crumple or Laundry numbers vs. 230 nm UV match factors for MEK extracts of black cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

18. Crumple or Laundry numbers vs. 240 nm UV match factors for MEK extracts of black cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

19. Crumple or Laundry numbers vs. 254 nm UV match factors for MEK extracts of black cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

20. Crumple or Laundry numbers vs. 275 nm UV match factors for MEK extracts of black cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

21. Crumple or Laundry numbers vs. MED match factors for MEK extracts of green cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

22. Crumple or Laundry numbers vs. 230 nm UV match factors for MEK extracts of green cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

23. Crumple or Laundry numbers vs. 240 nm UV match factors for MEK extracts of green cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

24. Crumple or Laundry numbers vs. 254 nm UV match factors for MEK extracts of green cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

25. Crumple or Laundry numbers vs. 275 nm UV match factors for MEK extracts of green cylinder wipe currency ink extracts; figure a, crumple numbers; figure b, laundry numbers.

Table I. Description of inks run. Ink#, NIST assigned ink #.

Ink#	Formulation	BEP ID#	color	Ink Type	Crumple/Laundry	
1	BK-62-RCA		black	paperwipe		
2	374017K	2-009-4749	black	currency		
3	374017K	2-009-4750	black	currency		
4	374017A	2-006-3749	black	currency		
5	374017K	2-009-4750	black	currency		
6	G-4717-RCA		green			
7	354033A	2-009-9262	green	currency		
8	354100J	2-009-8003	green	currency		
9	354033A	2-009-9267	green	currency		
10	354100J	2-009-8006	green	currency		
11	BK3795-3		black	paperwipe		
12	343186A		purple	postage		
13	363388A		brown	postage		
14	353377A		green	postage		
15	374017K	2-008-8007	black	currency		
16	374017K	2-009-0679	black	currency		
17	354100J	2-009-3505	green	currency		
18	354100J	2-009-3956	green	currency		
19	374017K	2-009-6124	black	currency	4.5	5.4
20	374017K	2-009-6394	black	currency		
21	374017K	2-009-6122	black	currency		
22	374017K	2-009-6403	black	currency		
23	374017K	2-009-6409	black	currency		
24	374017K	2-009-6412	black	currency		
25	374017K	2-009-6417	black	currency		
26	374017K	2-009-6399	black	currency		
27	SVD-1781			resin		
28		2-009-3773		postage		
29		2-010-0210		postage		
30		2-009-7465		postage		
31	374017K	2-009-6435	black	currency	6.0	5.0
32	374017K	2-009-6613	black	currency	6.0	5.3
33	374017K	2-009-6617	black	currency	6.0	4.3
34	374017K	2-009-6612	black	currency	6.0	4.8
35	374017K	2-009-6610	black	currency	5.9	5.1
36	374017K	2-009-6624	black	currency	6.0	4.4
37	374017K	2-009-6628	black	currency	5.3	5.0
38	374017K	2-009-6634	black	currency	6.0	4.7
39	374017K	2-009-6620	black	currency	6.0	4.0
40	374017K	2-009-6638	black	currency		
41	374017K	2-009-6635	black	currency	6.0	5.2
42	374017K	2-009-6912	black	currency	6.0	5.0
43	374017K	2-009-6926	black	currency	5.5	4.3
44	374017K	2-009-7010	black	currency	6.0	5.3
45	354033A	2-009-9253	green	currency	5.8	5.9
46	354033A	2-009-9265	green	currency		
47	354033A	2-009-9327	green	currency	6.0	5.3
48	354033A	2-009-9329	green	currency	6.0	5.6
49	354033A	2-009-9330	green	currency	6.0	5.5
50	354033A	2-009-9952	green	currency		

51	374017K	2-009-6994	black	currency	6.0	4.6
52	374017K	2-009-6995	black	currency	6.0	4.6
53	374017K	2-009-7032	black	currency	5.8	5.0
54	374017K	2-009-6124	black	currency		
55	374017K	2-009-6401	black	currency	5.3	5.4
56	374017K	2-009-6433	black	currency	6.0	5.2
57	374017K	2-009-7015	black	currency	6.0	4.9
58	374017K	2-009-7526	black	currency	6.0	4.3
59	374017K	2-009-7525	black	currency	4.8	4.6
60	374017K	2-009-7723	black	currency	6.0	4.5
61	374017K	2-009-7366	black	cur-press	5.4	4.0
62	374017K	2-009-7366	black	currency	5.4	4.0
63	374017K	2-009-7739	black	cur-press		
64	374017K	2-009-7739	black	currency		
65	374017K	2-009-7741	black	cur-press		
66	374017K	2-009-7741	black	currency		
67	374017K	2-009-7754	black	cur-press	2.8	5.1
68	374017K	2-009-7754	black	currency	2.8	5.1
69	374017K	2-009-7842	black	cur-press	5.5	5.4
70	374017K	2-009-7842	black	currency	5.5	5.4
71	374017K	2-009-7846	black	cur-press		
72	374017K	2-009-7846	black	currency		
73	374017K	2-009-8147	black	cur-press		
74	374017K	2-009-8147	black	currency		
75	374017K	2-009-7748	black	cur-press	6.0	5.4
76	374017K	2-009-7748	black	currency	6.0	5.4
77	374017K	2-009-7877	black	cur-press	4.6	4.3
78	374017K	2-009-7877	black	currency	4.6	4.3
79	374017K	2-009-8128	black	cur-press	6.0	4.3
80	374017K	2-009-8128	black	currency	6.0	4.3
81	374017K	2-009-8133	black	cur-press		
82	374017K	2-009-8133	black	currency		
83	374017K	2-009-6124	black	currency		
84	374017K	2-009-6401	black	currency		
85	374017K	2-009-6433	black	currency		
86	374017K	2-009-6994	black	currency		
87	374017K	2-009-6995	black	currency		
88	374017K	2-009-7015	black	currency		
89	374017K	2-009-7032	black	currency		
90	374017K	2-009-7525	black	currency		
91	374017K	2-009-7526	black	currency		
92	374017K	2-009-7723	black	currency		
93	374017K	2-009-8162	black	cur-press	6.0	5.0
94	374017K	2-009-8500	black	cur-press	5.8	4.7
95	374017K	2-009-8517	black	cur-press	6.0	4.7
96	354033A	2-009-9256	green	currency		
97	354033A	2-009-9248	green	currency	5.8	5.5
98	354033A	2-009-9361	green	currency	6.0	6.0
99	354033A	2-009-9412	green	currency	6.0	5.9
100	354033A	2-009-9440	green	currency	6.0	6.0
101	354033A	2-009-9559	green	currency	6.0	5.8
102	354033A	2-009-9835	green	currency	6.0	5.8
103	354033A	2-009-9847	green	currency	6.0	5.9
104	354033A	2-009-9954	green	currency	5.9	5.6

105	354033A	2-009-9979	green	currency	6.0	5.7
106	354033A	2-010-1137	green	currency		
107	354033A	2-010-1138	green	currency		
108	354033A	2-010-1293	green	currency		
109	374017K	2-009-6599	black	currency	5.4	5.2
110	374017K	2-009-6600	black	currency	6.0	5.6
111	374017K	2-009-7004	black	currency	5.8	4.8
112	374017K	2-009-7375	black	currency	5.8	4.1
113	374017K	2-009-7385	black	currency	6.0	4.4
114	374017K	2-009-7758	black	currency	6.0	4.3
115	374017K	2-009-7847	black	currency	5.8	5.0
116	374017K	2-009-8144	black	currency		
117	374017K	2-009-8165	black	currency		
118	374017K	2-009-6433	black	currency		
119	374017K	2-009-6994	black	currency		
120	374017K	2-009-6995	black	currency		
121	374017K	2-009-7015	black	currency		
122	374017K	2-009-7366	black	currency		
123	374017K	2-009-8147	black	currency	6.0	5.2
124	354033A	2-009-0690	green	currency	5.8	5.7
125	354033A	2-010-0733	green	currency	6.0	5.6
126	354033A	2-010-0907	green	currency	5.8	4.9
127	354033A	2-010-0913	green	currency	6.0	5.0
128	354033A	2-010-1294	green	currency	5.5	5.6
129	354033A	2-010-1406	green	currency	5.5	5.0
130	354033A	2-010-1427	green	currency	5.8	5.2
131	354033A	2-010-1682	green	currency	5.5	5.8
132	354033A	2-010-3404	green	currency	6.0	5.2
133	354033A	2-010-4155	green	currency	6.0	5.4
134	354033A	2-010-4168	green	currency	5.4	5.5
135	354033A	2-009-9361	green	currency		
136	354033A	2-009-9424	green	currency	5.5	5.9
137	354033A	2-009-9440	green	currency		
138	354033A	2-009-9585	green	currency	5.8	5.6
139	354033A	2-009-9550	green	currency	6.0	5.8

Table II. Chromatographic conditions of ink extract runs. SEC#, NIST GPC identification; Sample, NIST ink # or descriotion; Column, 1 for old column or 2 for replacement column; BHT/flow, flow solvent; BHT/ext, extraction solvent; Rerun of/ old samp, rerun of aged sample; Isco, replacement pump, MED/upg, upgrade of MED detector; 2nd UV, use of a second UV detector at 254 nm.

SEC#	Sample	Column	BHT flow	BHT ext	Rerun of old samp	Isco	MED upg	2nd UV
4670	blank	1	-	-	-	-	-	-
4671	1	1	-	-	-	-	-	-
4672	1	1	-	-	-	-	-	-
4673	1	1	-	-	-	-	-	-
4674	1	1	-	-	-	-	-	-
4675	2	1	-	-	-	-	-	-
4676	2	1	-	-	-	-	-	-
4677	2	1	-	-	-	-	-	-
4678	2	1	-	-	-	-	-	-
4679	3	1	-	-	-	-	-	-
4680	3	1	-	-	-	-	-	-
4681	3	1	-	-	-	-	-	-
4682	3	1	-	-	-	-	-	-
4683	4	1	-	-	-	-	-	-
4684	4	1	-	-	-	-	-	-
4685	4	1	-	-	-	-	-	-
4686	4	1	-	-	-	-	-	-
4687	5	1	-	-	-	-	-	-
4688	5	1	-	-	-	-	-	-
4689	5	1	-	-	-	-	-	-
4690	5	1	-	-	-	-	-	-
4691	6	1	-	-	-	-	-	-
4692	6	1	-	-	-	-	-	-
4693	6	1	-	-	-	-	-	-
4694	6	1	-	-	-	-	-	-
4695	7	1	-	-	-	-	-	-
4696	7	1	-	-	-	-	-	-
4697	7	1	-	-	-	-	-	-
4698	7	1	-	-	-	-	-	-
4699	PS standards	1	-	-	-	-	-	-
4700	8	1	-	-	-	-	-	-
4701	8	1	-	-	-	-	-	-
4702	8	1	-	-	-	-	-	-
4703	8	1	-	-	-	-	-	-
4704	9	1	-	-	-	-	-	-
4705	9	1	-	-	-	-	-	-
4706	9	1	-	-	-	-	-	-
4707	9	1	-	-	-	-	-	-
4708	10	1	-	-	-	-	-	-
4709	10	1	-	-	-	-	-	-
4710	10	1	-	-	-	-	-	-
4711	10	1	-	-	-	-	-	-
4712	11	1	-	-	-	-	-	-
4713	11	1	-	-	-	-	-	-

4714	11	1	-	-	-	-	-	-
4715	11	1	-	-	-	-	-	-
4716	12	1	-	-	-	-	-	-
4717	12	1	-	-	-	-	-	-
4718	12	1	-	-	-	-	-	-
4719	12	1	-	-	-	-	-	-
4720	13	1	-	-	-	-	-	-
4721	13	1	-	-	-	-	-	-
4722	13	1	-	-	-	-	-	-
4723	13	1	-	-	-	-	-	-
4724	14	1	-	-	-	-	-	-
4725	14	1	-	-	-	-	-	-
4726	14	1	-	-	-	-	-	-
4727	14	1	-	-	-	-	-	-
4734	blank	1	-	-	-	-	-	-
4735	1	1	-	-	-	-	-	-
4736	2	1	-	-	-	-	-	-
4737	3	1	-	-	-	-	-	-
4738	4	1	-	-	-	-	-	-
4739	5	1	-	-	-	-	-	-
4740	6	1	-	-	-	-	-	-
4741	7	1	-	-	-	-	-	-
4742	PS standards	1	-	-	-	-	-	-
4743	8	1	-	-	-	-	-	-
4744	9	1	-	-	-	-	-	-
4745	10	1	-	-	-	-	-	-
4746	11	1	-	-	-	-	-	-
4747	12	1	-	-	-	-	-	-
4748	13	1	-	-	-	-	-	-
4749	14	1	-	-	-	-	-	-
4750	blank	1	-	-	-	-	-	-
4751	1	1	-	-	-	-	-	-
4752	2	1	-	-	-	-	-	-
4753	3	1	-	-	-	-	-	-
4754	4	1	-	-	-	-	-	-
4755	5	1	-	-	-	-	-	-
4756	6	1	-	-	-	-	-	-
4757	7	1	-	-	-	-	-	-
4758	PS standards	1	-	-	-	-	-	-
4759	8	1	-	-	-	-	-	-
4760	9	1	-	-	-	-	-	-
4761	10	1	-	-	-	-	-	-
4762	11	1	-	-	-	-	-	-
4763	12	1	-	-	-	-	-	-
4764	13	1	-	-	-	-	-	-
4765	14	1	-	-	-	-	-	-
4795	blank	1	-	-	-	-	-	-
4796	15	1	-	-	-	-	-	-
4797	15	1	-	-	-	-	-	-
4798	15	1	-	-	-	-	-	-
4799	15	1	-	-	-	-	-	-
4800	15	1	-	-	-	-	-	-
4801	16	1	-	-	-	-	-	-
4802	16	1	-	-	-	-	-	-

4803	16	1	-	-	-	-	-	-
4804	16	1	-	-	-	-	-	-
4805	16	1	-	-	-	-	-	-
4806	17	1	-	-	-	-	-	-
4807	17	1	-	-	-	-	-	-
4808	17	1	-	-	-	-	-	-
4809	17	1	-	-	-	-	-	-
4810	17	1	-	-	-	-	-	-
4811	18	1	-	-	-	-	-	-
4812	18	1	-	-	-	-	-	-
4813	18	1	-	-	-	-	-	-
4814	18	1	-	-	-	-	-	-
4815	18	1	-	-	-	-	-	-
4816	19	1	-	-	-	-	-	-
4817	19	1	-	-	-	-	-	-
4818	19	1	-	-	-	-	-	-
4819	19	1	-	-	-	-	-	-
4820	19	1	-	-	-	-	-	-
4821	20	1	-	-	-	-	-	-
4822	20	1	-	-	-	-	-	-
4823	20	1	-	-	-	-	-	-
4824	20	1	-	-	-	-	-	-
4825	20	1	-	-	-	-	-	-
4826	PS standards	1	-	-	-	-	-	-
4827	21	1	-	-	-	-	-	-
4828	21	1	-	-	-	-	-	-
4829	21	1	-	-	-	-	-	-
4830	21	1	-	-	-	-	-	-
4831	21	1	-	-	-	-	-	-
4832	22	1	-	-	-	-	-	-
4833	22	1	-	-	-	-	-	-
4834	22	1	-	-	-	-	-	-
4835	22	1	-	-	-	-	-	-
4836	22	1	-	-	-	-	-	-
4837	23	1	-	-	-	-	-	-
4838	23	1	-	-	-	-	-	-
4839	23	1	-	-	-	-	-	-
4840	23	1	-	-	-	-	-	-
4841	23	1	-	-	-	-	-	-
4842	24	1	-	-	-	-	-	-
4843	24	1	-	-	-	-	-	-
4844	24	1	-	-	-	-	-	-
4845	24	1	-	-	-	-	-	-
4846	24	1	-	-	-	-	-	-
4847	25	1	-	-	-	-	-	-
4848	25	1	-	-	-	-	-	-
4849	25	1	-	-	-	-	-	-
4850	25	1	-	-	-	-	-	-
4851	25	1	-	-	-	-	-	-
4852	26	1	-	-	-	-	-	-
4853	26	1	-	-	-	-	-	-
4854	26	1	-	-	-	-	-	-
4855	26	1	-	-	-	-	-	-
4856	26	1	-	-	-	-	-	-

4857	27	1	-	-	-	-	-	-
4858	PS standards	1	-	-	-	-	-	-
4859	blank	1	-	-	-	-	-	-
4860	15	1	-	-	-	-	-	-
4861	16	1	-	-	-	-	-	-
4862	17	1	-	-	-	-	-	-
4863	18	1	-	-	-	-	-	-
4864	19	1	-	-	-	-	-	-
4865	20	1	-	-	-	-	-	-
4866	PS standards	1	-	-	-	-	-	-
4867	21	1	-	-	-	-	-	-
4868	22	1	-	-	-	-	-	-
4869	23	1	-	-	-	-	-	-
4870	24	1	-	-	-	-	-	-
4871	25	1	-	-	-	-	-	-
4872	26	1	-	-	-	-	-	-
4873	27	1	-	-	-	-	-	-
4874	PS standards	1	-	-	-	-	-	-
4876	blank	1	-	-	-	-	-	-
4877	28	1	-	-	-	-	-	-
4878	28	1	-	-	-	-	-	-
4879	28	1	-	-	-	-	-	-
4880	28	1	-	-	-	-	-	-
4881	28	1	-	-	-	-	-	-
4882	29	1	-	-	-	-	-	-
4883	29	1	-	-	-	-	-	-
4884	29	1	-	-	-	-	-	-
4885	29	1	-	-	-	-	-	-
4886	29	1	-	-	-	-	-	-
4887	30	1	-	-	-	-	-	-
4888	30	1	-	-	-	-	-	-
4889	30	1	-	-	-	-	-	-
4890	30	1	-	-	-	-	-	-
4891	30	1	-	-	-	-	-	-
4892	PS standards	1	-	-	-	-	-	-
4978	blank	1	-	-	-	-	-	-
4979	31	1	-	-	-	-	-	-
4980	31	1	-	-	-	-	-	-
4981	31	1	-	-	-	-	-	-
4982	31	1	-	-	-	-	-	-
4983	32	1	-	-	-	-	-	-
4984	32	1	-	-	-	-	-	-
4985	32	1	-	-	-	-	-	-
4986	32	1	-	-	-	-	-	-
4987	33	1	-	-	-	-	-	-
4988	33	1	-	-	-	-	-	-
4989	33	1	-	-	-	-	-	-
4990	33	1	-	-	-	-	-	-
4991	34	1	-	-	-	-	-	-
4992	34	1	-	-	-	-	-	-
4993	34	1	-	-	-	-	-	-
4994	34	1	-	-	-	-	-	-
4995	35	1	-	-	-	-	-	-
4996	35	1	-	-	-	-	-	-

4997	35	1	-	-	-	-	-	-
4998	35	1	-	-	-	-	-	-
4999	36	1	-	-	-	-	-	-
5000	36	1	-	-	-	-	-	-
5001	36	1	-	-	-	-	-	-
5002	36	1	-	-	-	-	-	-
5003	37	1	-	-	-	-	-	-
5004	37	1	-	-	-	-	-	-
5005	37	1	-	-	-	-	-	-
5006	37	1	-	-	-	-	-	-
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5011	39	1	-	-	-	-	-	-
5012	39	1	-	-	-	-	-	-
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5048	42	1	-	-	-	-	-	-
5049	43	1	-	-	-	-	-	-
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5051	PS standards	1	-	-	-	-	-	-
5121	PS standards	1	-	-	-	-	+	-
5122	31	1	-	-	-	-	+	-
5123	32	1	-	-	-	-	+	-
5124	33	1	-	-	-	-	+	-
5125	34	1	-	-	-	-	+	-
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5128	37	1	-	-	-	-	+	-
5129	38	1	-	-	-	-	+	-
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5131	40	1	-	-	-	-	+	-
5132	41	1	-	-	-	-	+	-
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5038	PS standards	1	-	-	-	-	+	-
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5073	48	1	-	-	-	-	+	-
5074	48	1	-	-	-	-	+	-

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5111	67	1	-	-	-	-	+	-
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5127	75	1	-	-	-	-	+	-
5128	75	1	-	-	-	-	+	-

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5131	77	1	-	-	-	-	+	-
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5164	93	1	-	-	-	-	+	-
5165	94	1	-	-	-	-	+	-
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5167	blank	1	-	-	-	-	+	-
5168	PS standards	1	-	-	-	-	+	-
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5172	45	1	-	-	-	-	+	-
5173	46	1	-	-	-	-	+	-
5174	46	1	-	-	-	-	+	-
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5180	49	1	-	-	-	-	+	-
5181	50	1	-	-	-	-	+	-
5182	50	1	-	-	-	-	+	-
5183	blank	1	-	-	-	-	+	-

5184	blank	1	-	-	-	-	+	-
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5187	45	1	-	-	-	-	+	-
5188	46	1	-	-	-	-	+	-
5189	46	1	-	-	-	-	+	-
5190	47	1	-	-	-	-	+	-
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5201	52	1	-	-	-	-	+	-
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5204	blank	1	-	-	-	-	+	-
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5210	38	1	-	-	+	-	+	-
5211	50	1	-	-	+	-	+	-
5227	blank	1	-	-	+	-	+	-
5228	PS standards	1	-	-	+	-	+	-
5229	3	1	-	-	+	-	+	-
5230	22	1	-	-	+	-	+	-
5231	38	1	-	-	+	-	+	-
5232	47	1	-	-	+	-	+	-
5233	38	1	-	-	+	-	+	-
5234	blank	2	-	-	+	-	+	-
5235	PS standards	2	-	-	+	-	+	-
5236	3	2	-	-	+	-	+	-
5237	22	2	-	-	+	-	+	-
5238	38	2	-	-	+	-	+	-
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5240	38	2	-	-	+	-	+	-
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5242	PS standards	2	-	-	+	-	+	-
5243	3	2	-	-	+	-	+	-
5244	22	2	-	-	+	-	+	-
5245	38	2	-	-	+	-	+	-
5246	47	2	-	-	+	-	+	-
5247	38	2	-	-	+	-	+	-
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5249	PS standards	2	-	-	+	-	+	-
5250	3	2	-	-	+	-	+	-
5251	22	2	-	-	+	-	+	-
5252	38	2	-	-	+	-	+	-

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5255	blank	2	-	-	-	-	+	-
5256	PS standards	2	-	-	-	-	+	-
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5278	55	2	-	-	-	-	+	-
5279	56	2	-	-	-	-	+	-
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5313	60	2	-	-	-	-	+	-
5314	PS standards	2	-	-	-	-	+	-
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5351	55	2	-	-	-	-	+	-
5398	PS standards	2	-	+	-	-	+	-
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5400	62	2	-	+	-	-	+	-
5401	63	2	-	+	-	-	+	-
5402	64	2	-	+	-	-	+	-
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5409	71	2	-	+	-	-	+	-
5410	72	2	-	+	-	-	+	-
5414	73	2	-	+	-	-	+	-
5415	74	2	-	+	-	-	+	-
5416	PS standards	2	-	+	-	-	+	-
5417	75	2	-	+	-	-	+	-
5418	76	2	-	+	-	-	+	-
5419	77	2	-	+	-	-	+	-
5420	78	2	-	+	-	-	+	-
5421	79	2	-	+	-	-	+	-

5422	80	2	-	+	-	-	+	-
5423	81	2	-	+	-	-	+	-
5424	82	2	-	+	-	-	+	-
5425	blank	2	-	+	-	-	+	-
5427	82	2	-	+	-	-	+	-
5428	83	2	-	+	-	-	+	-
5429	84	2	-	+	-	-	+	-
5430	85	2	-	+	-	-	+	-
5431	86	2	-	+	-	-	+	-
5432	87	2	-	+	-	-	+	-
5433	88	2	-	+	-	-	+	-
5434	89	2	-	+	-	-	+	-
5435	PS standards	2	-	+	-	-	+	-
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5437	76	2	-	+	-	-	+	-
5438	77	2	-	+	-	-	+	-
5439	78	2	-	+	-	-	+	-
5440	79	2	-	+	-	-	+	-
5441	80	2	-	+	-	-	+	-
5442	81	2	-	+	-	-	+	-
5443	82	2	-	+	-	-	+	-
5444	blank	2	-	+	-	-	+	-
5457	PS standards	2	-	+	-	-	+	-
5458	83	2	-	+	-	-	+	-
5459	84	2	-	+	-	-	+	-
5460	85	2	-	+	-	-	+	-
5461	86	2	-	+	-	-	+	-
5462	87	2	-	+	-	-	+	-
5463	88	2	-	+	-	-	+	-
5464	89	2	-	+	-	-	+	-
5465	90	2	-	+	-	-	+	-
5466	91	2	-	+	-	-	+	-
5467	92	2	-	+	-	-	+	-
5468	93	2	-	+	-	-	+	-
5469	94	2	-	+	-	-	+	-
5470	95	2	-	+	-	-	+	-
5471	96	2	-	+	-	-	+	-
5472	97	2	-	+	-	-	+	-
5479	PS standards	2	-	+	-	-	+	-
5480	71	2	-	+	-	-	+	-
5481	72	2	-	+	-	-	+	-
5482	73	2	-	+	-	-	+	-
5483	74	2	-	+	-	-	+	-
5484	75	2	-	+	-	-	+	-
5485	76	2	-	+	-	-	+	-
5486	77	2	-	+	-	-	+	-
5487	78	2	-	+	-	-	+	-
5488	79	2	-	+	-	-	+	-
5489	80	2	-	+	-	-	+	-
5490	81	2	-	+	-	-	+	-
5491	82	2	-	+	-	-	+	-
5492	83	2	-	+	-	-	+	-
5493	blank	2	-	+	-	-	+	-
5498	PS standards	2	-	+	-	-	+	-

5499	95	2	-	+	-	-	+	-
5500	95	2	-	+	-	-	+	-
5501	95	2	-	+	-	-	+	-
5502	95	2	-	+	-	-	+	-
5503	95	2	-	+	-	-	+	-
5504	95	2	-	+	-	-	+	-
5505	95	2	-	+	-	-	+	-
5506	95	2	-	+	-	-	+	-
5507	95	2	-	+	-	-	+	-
5508	95	2	-	+	-	-	+	-
5509	95	2	-	+	-	-	+	-
5510	95	2	-	+	-	-	+	-
5511	95	2	-	+	-	-	+	-
5512	95	2	-	+	-	-	+	-
5513	95	2	-	+	-	-	+	-
5514	95	2	-	+	-	-	+	-
5515	95	2	-	+	-	-	+	-
5516	blank	2	-	+	-	-	+	-
5517	96	2	-	+	-	-	+	-
5518	97	2	-	+	-	-	+	-
5519	98	2	-	+	-	-	+	-
5520	99	2	-	+	-	-	+	-
5521	100	2	-	+	-	-	+	-
5522	101	2	-	+	-	-	+	-
5523	102	2	-	+	-	-	+	-
5524	103	2	-	+	-	-	+	-
5525	104	2	-	+	-	-	+	-
5526	105	2	-	+	-	-	+	-
5527	106	2	-	+	-	-	+	-
5528	107	2	-	+	-	-	+	-
5529	108	2	-	+	-	-	+	-
5530	blank	2	-	+	-	-	+	-
5533	blank	2	-	+	-	-	+	-
5534	96	2	-	+	-	-	+	-
5535	97	2	-	+	-	-	+	-
5536	98	2	-	+	-	-	+	-
5537	99	2	-	+	-	-	+	-
5538	100	2	-	+	-	-	+	-
5539	101	2	-	+	-	-	+	-
5540	102	2	-	+	-	-	+	-
5541	103	2	-	+	-	-	+	-
5542	104	2	-	+	-	-	+	-
5543	105	2	-	+	-	-	+	-
5544	106	2	-	+	-	-	+	-
5545	107	2	-	+	-	-	+	-
5546	108	2	-	+	-	-	+	-
5547	blank	2	-	+	-	-	+	-
5636	99	2	-	+	-	+	+	+
5637	99	2	-	+	-	+	+	+
5638	99	2	-	+	-	+	+	+
5639	99	2	-	+	-	+	+	+
5640	99	2	-	+	-	+	+	+
5641	99	2	-	+	-	+	+	+
5642	99	2	-	+	-	+	+	+

5643	99	2	-	+	-	+	+	+
5644	99	2	-	+	-	+	+	+
5645	76	2	-	+	-	+	+	+
5646	76	2	-	+	-	+	+	+
5647	76	2	-	+	-	+	+	+
5648	76	2	-	+	-	+	+	+
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5650	76	2	-	+	-	+	+	+
5651	76	2	-	+	-	+	+	+
5652	76	2	-	+	-	+	+	+
5654	76 + DABCO)	2	-	+	-	+	+	+
5655	76 + DABCO)	2	-	+	-	+	+	+
5656	76 + DABCO)	2	-	+	-	+	+	+
5657	76 + DABCO)	2	-	+	-	+	+	+
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5664	76 + DABCO)	2	-	+	-	+	+	+
5665	76 + DABCO)	2	-	+	-	+	+	+
5666	76 + 3 X BHT	2	-	+	-	+	+	+
5667	76 + 3 X BHT	2	-	+	-	+	+	+
5668	76 + 3 X BHT	2	-	+	-	+	+	+
5669	76 + 3 X BHT	2	-	+	-	+	+	+
5670	76 + 3 X BHT	2	-	+	-	+	+	+
5671	76 + 3 X BHT	2	-	+	-	+	+	+
5672	76 + 3 X BHT	2	-	+	-	+	+	+
5673	76 + 3 X BHT	2	-	+	-	+	+	+
5674	76 + 3 X BHT	2	-	+	-	+	+	+
5675	109	2	-	+	-	+	+	+
5676	110	2	-	+	-	+	+	+
5677	111	2	-	+	-	+	+	+
5678	112	2	-	+	-	+	+	+
5679	113	2	-	+	-	+	+	+
5680	114	2	-	+	-	+	+	+
5681	115	2	-	+	-	+	+	+
5682	116	2	-	+	-	+	+	+
5683	117	2	-	+	-	+	+	+
5684	118	2	-	+	-	+	+	+
5685	119	2	-	+	-	+	+	+
5686	120	2	-	+	-	+	+	+
5687	121	2	-	+	-	+	+	+
5688	122	2	-	+	-	+	+	+
5689	123	2	-	+	-	+	+	+
5690	PS standards	2	-	+	-	+	+	+
5691	109	2	+	+	-	+	+	+
5692	110	2	+	+	-	+	+	+
5693	111	2	+	+	-	+	+	+
5694	112	2	+	+	-	+	+	+
5695	113	2	+	+	-	+	+	+
5696	114	2	+	+	-	+	+	+
5697	115	2	+	+	-	+	+	+

5698	116	2	+	+	-	+	+	+
5699	117	2	+	+	-	+	+	+
5700	118	2	+	+	-	+	+	+
5701	119	2	+	+	-	+	+	+
5702	120	2	+	+	-	+	+	+
5703	121	2	+	+	-	+	+	+
5704	122	2	+	+	-	+	+	+
5705	123	2	+	+	-	+	+	+
5706	PS standards	2	+	+	-	+	+	+
5765	139	1	+	MEK	-	+	+	+
5766	117	1	+	MEK	-	+	+	-
5767	117	1	+	MEK	-	+	+	-
5768	117	1	+	MEK	-	+	+	-
5769	117	1	+	MEK	-	+	+	-
5770	117	1	+	MEK	-	+	+	-
5771	117	1	+	MEK	-	+	+	-
5772	117	1	+	MEK	-	+	+	-
5773	117	1	+	MEK	-	+	+	-
5774	117	1	+	MEK	-	+	+	-
5800	61	1	+	MEK	-	+	+	-
5801	62	1	+	MEK	-	+	+	-
5802	63	1	+	MEK	-	+	+	-
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5804	65	1	+	MEK	-	+	+	-
5805	66	1	+	MEK	-	+	+	-
5806	67	1	+	MEK	-	+	+	-
5807	68	1	+	MEK	-	+	+	-
5808	71	1	+	MEK	-	+	+	-
5809	72	1	+	MEK	-	+	+	-
5810	73	1	+	MEK	-	+	+	-
5811	74	1	+	MEK	-	+	+	-
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5813	80	1	+	MEK	-	+	+	-
5814	69	1	+	MEK	-	+	+	-
5815	76	1	+	MEK	-	+	+	-
5816	78	1	+	MEK	-	+	+	-
5817	blank	1	+	MEK	-	+	+	-
5818	51	1	+	MEK	-	+	+	-
5819	52	1	+	MEK	-	+	+	-
5820	53	1	+	MEK	-	+	+	-
5821	55	1	+	MEK	-	+	+	-
5822	56	1	+	MEK	-	+	+	-
5823	57	1	+	MEK	-	+	+	-
5824	58	1	+	MEK	-	+	+	-
5825	59	1	+	MEK	-	+	+	-
5826	60	1	+	MEK	-	+	+	-
5827	70	1	+	MEK	-	+	+	-
5828	75	1	+	MEK	-	+	+	-
5829	77	1	+	MEK	-	+	+	-
5830	81	1	+	MEK	-	+	+	-
5831	82	1	+	MEK	-	+	+	-
5836	124	1	+	MEK	-	+	+	-
5837	125	1	+	MEK	-	+	+	-
5838	126	1	+	MEK	-	+	+	-

5839	127	1	+	MEK	-	+	+	-
5840	128	1	+	MEK	-	+	+	-
5841	129	1	+	MEK	-	+	+	-
5842	130	1	+	MEK	-	+	+	-
5843	131	1	+	MEK	-	+	+	-
5844	132	1	+	MEK	-	+	+	-
5845	133	1	+	MEK	-	+	+	-
5846	134	1	+	MEK	-	+	+	-
5847	135	1	+	MEK	-	+	+	-
5848	136	1	+	MEK	-	+	+	-
5849	137	1	+	MEK	-	+	+	-
5850	138	1	+	MEK	-	+	+	-

Figure 1. MED Signal Before and After Upgrade

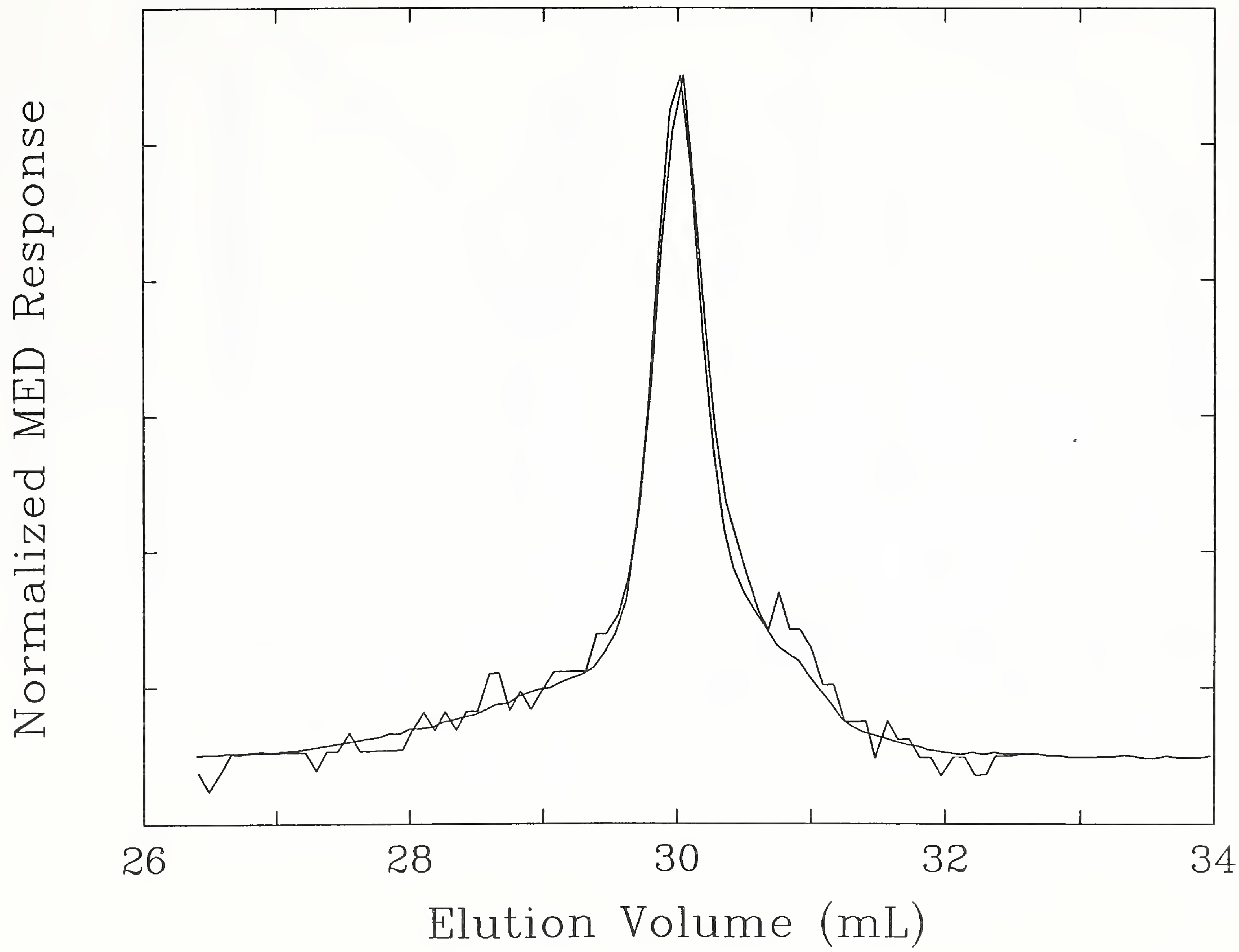


Figure 2. 254 nm UV Signal of 3 Ink Extracts

Figure 2a. Unshifted

Figure 2b. Shifted to Markers

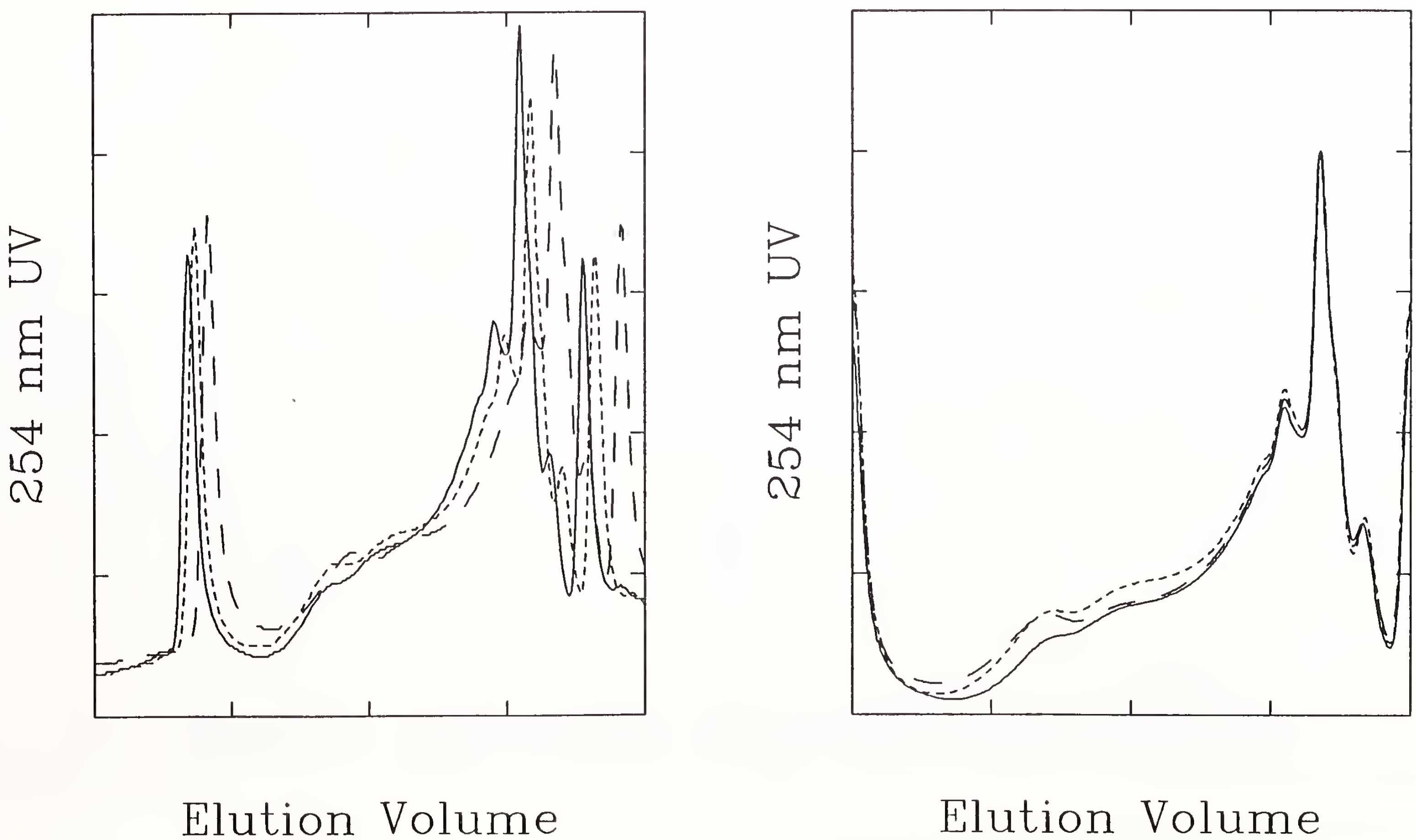


Figure 3. 254 nm UV Signal from Black Ink Extracts

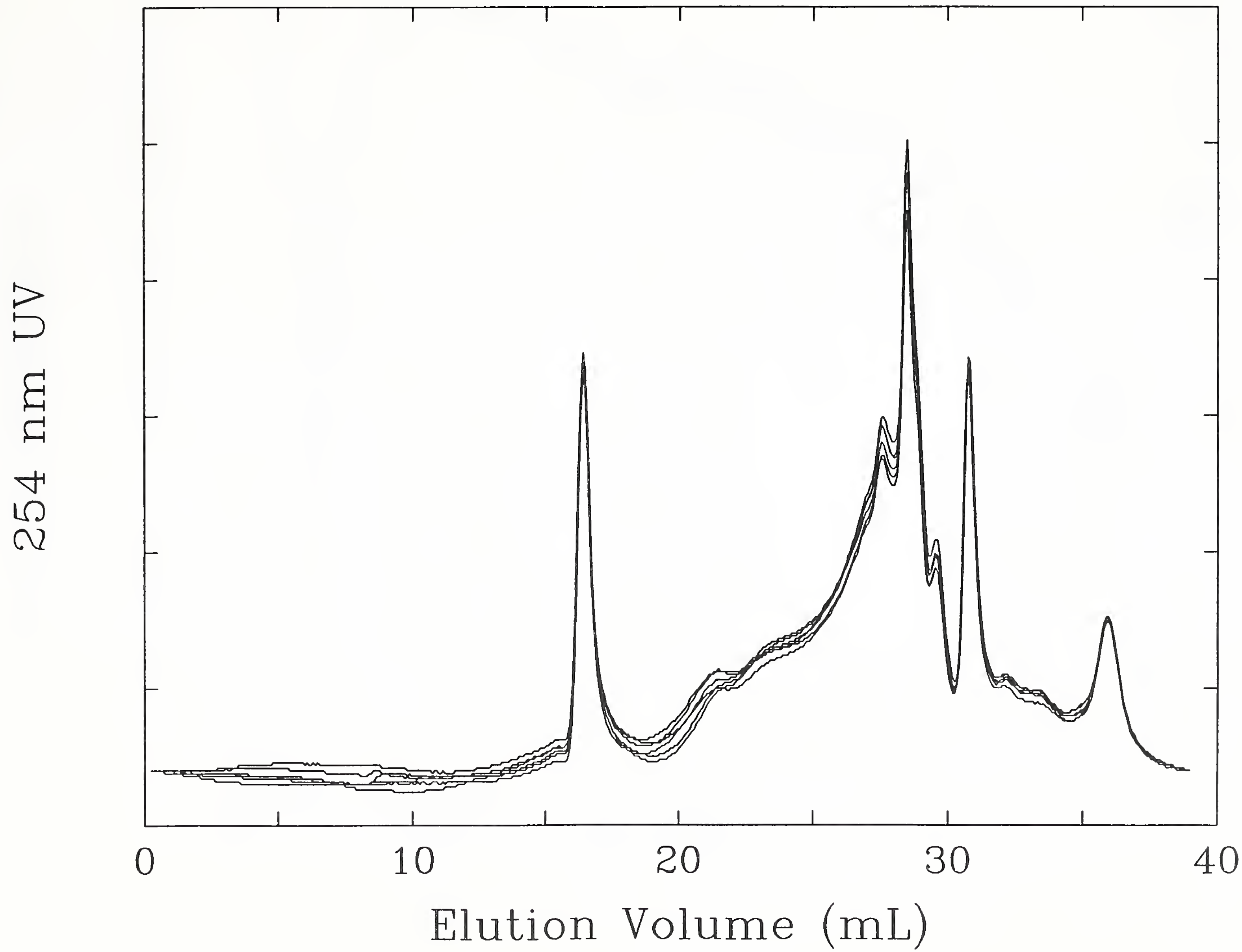


Figure 4. Aging of Ink Extract in THF without BHT

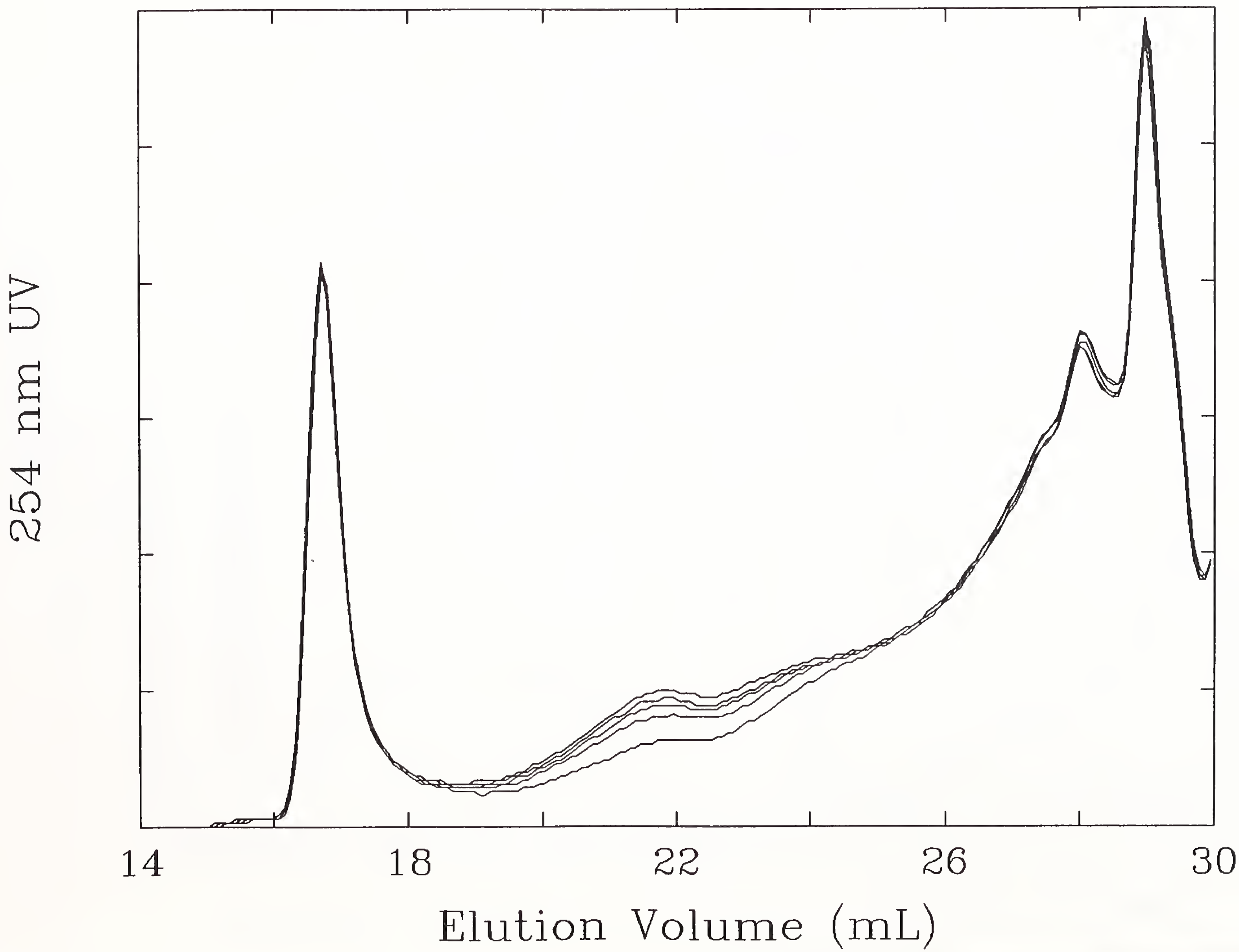
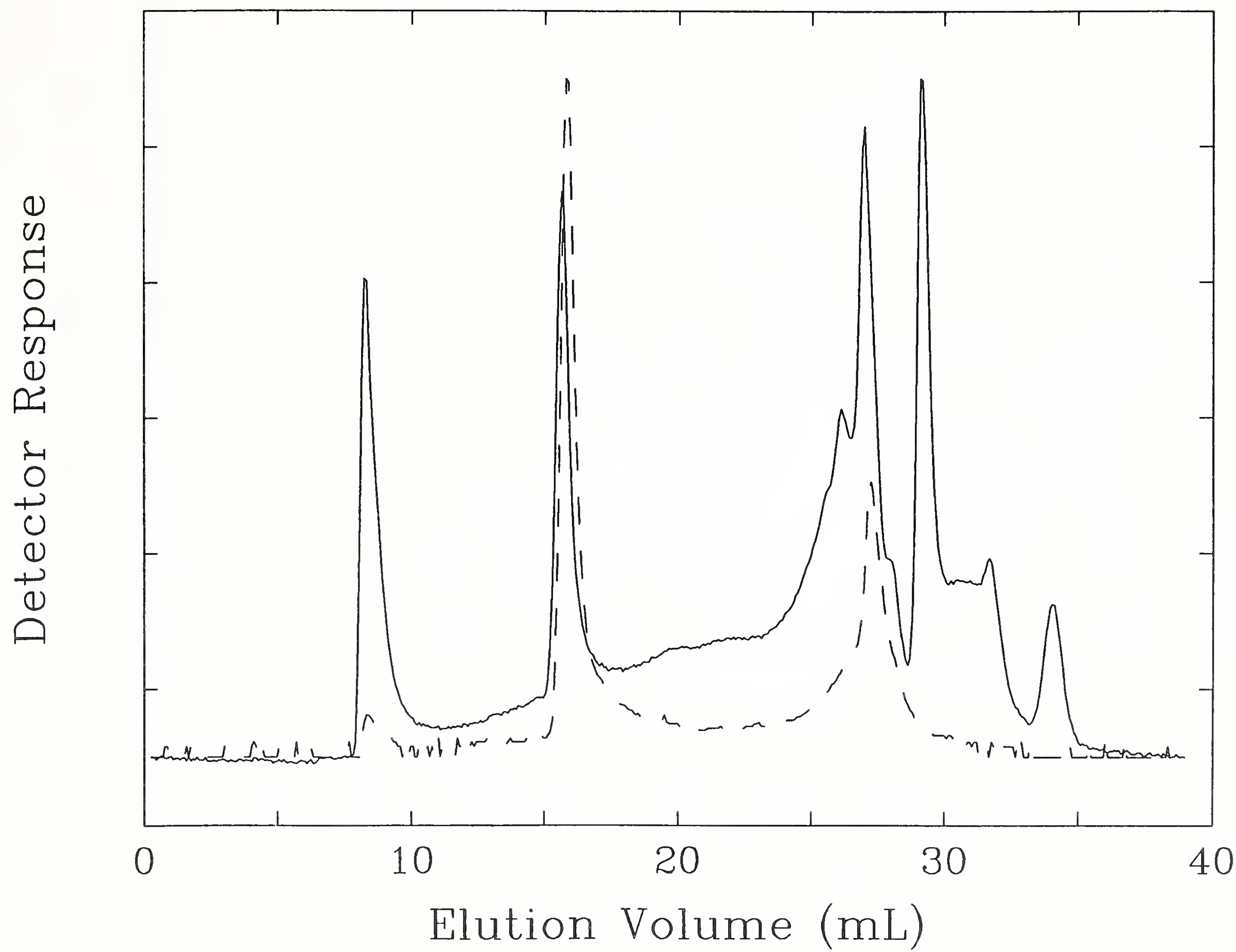


Figure 5. UV and MED Response Showing Early Peak



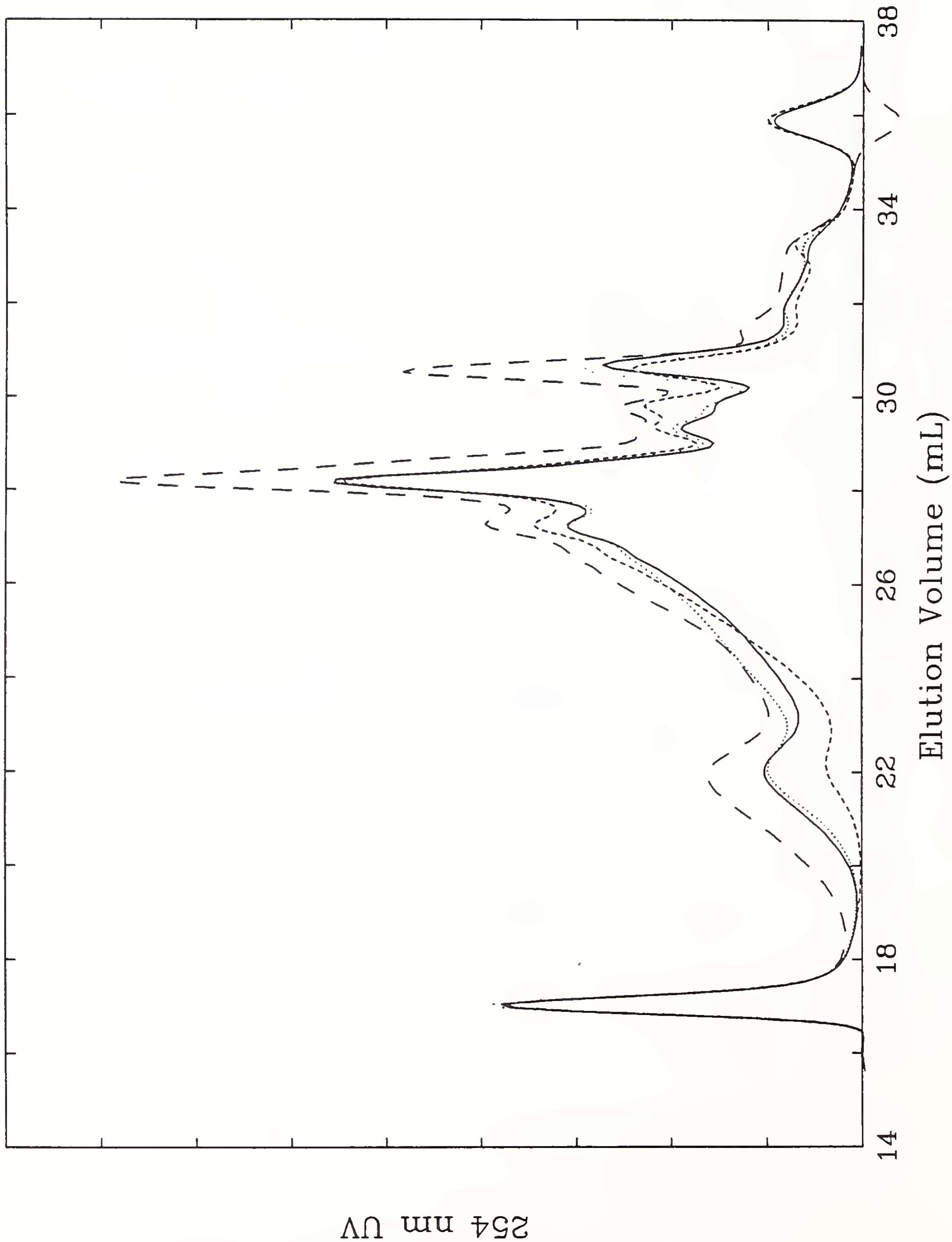


Figure 6. GPC of Black and Green Cylinder Wipe Currency Inks

Figure 7. Three Pairs of Press Samples and Retains

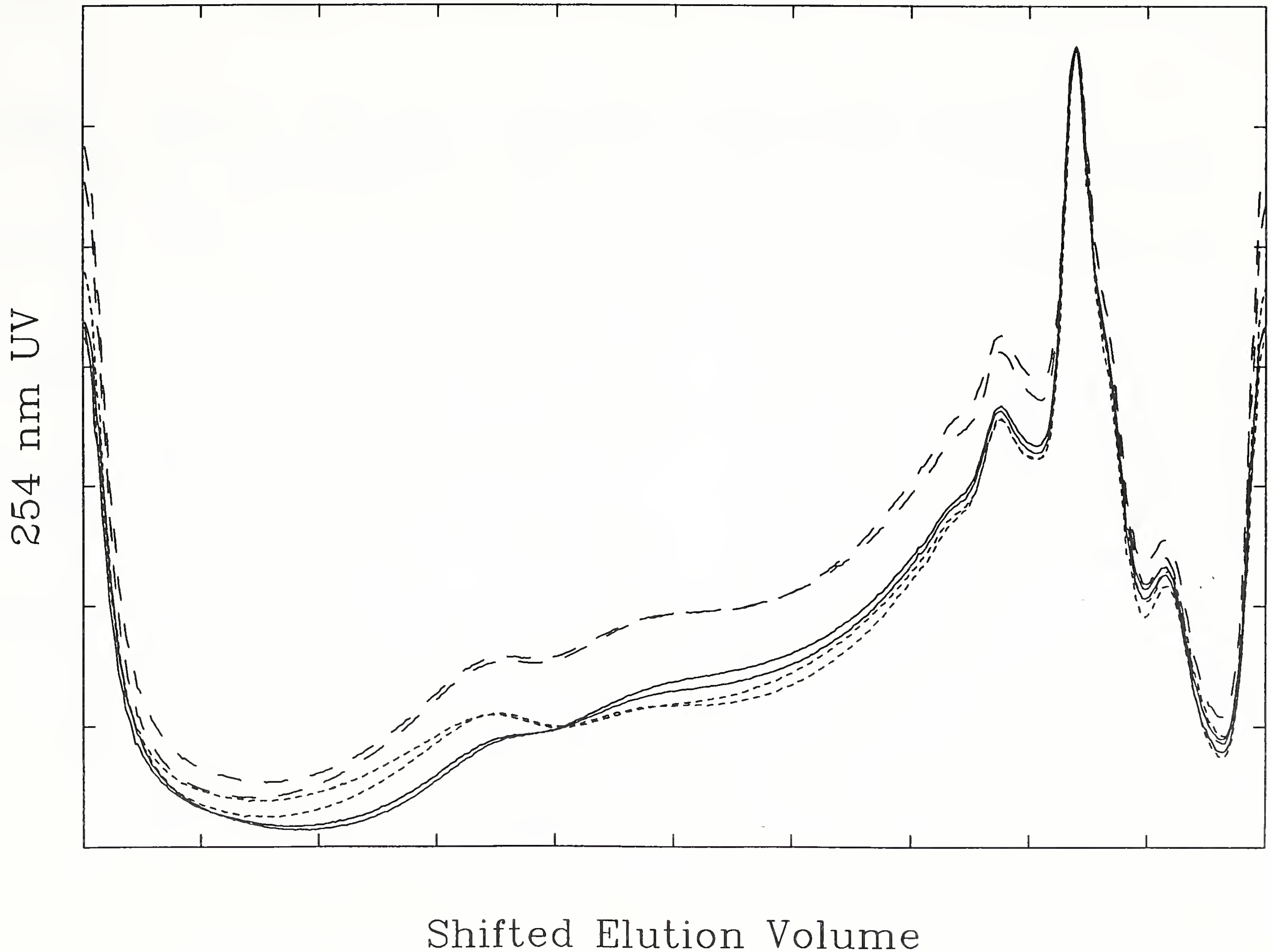


Figure 8. Average Match Factors of Press-Retain Pairs and all Combinations.

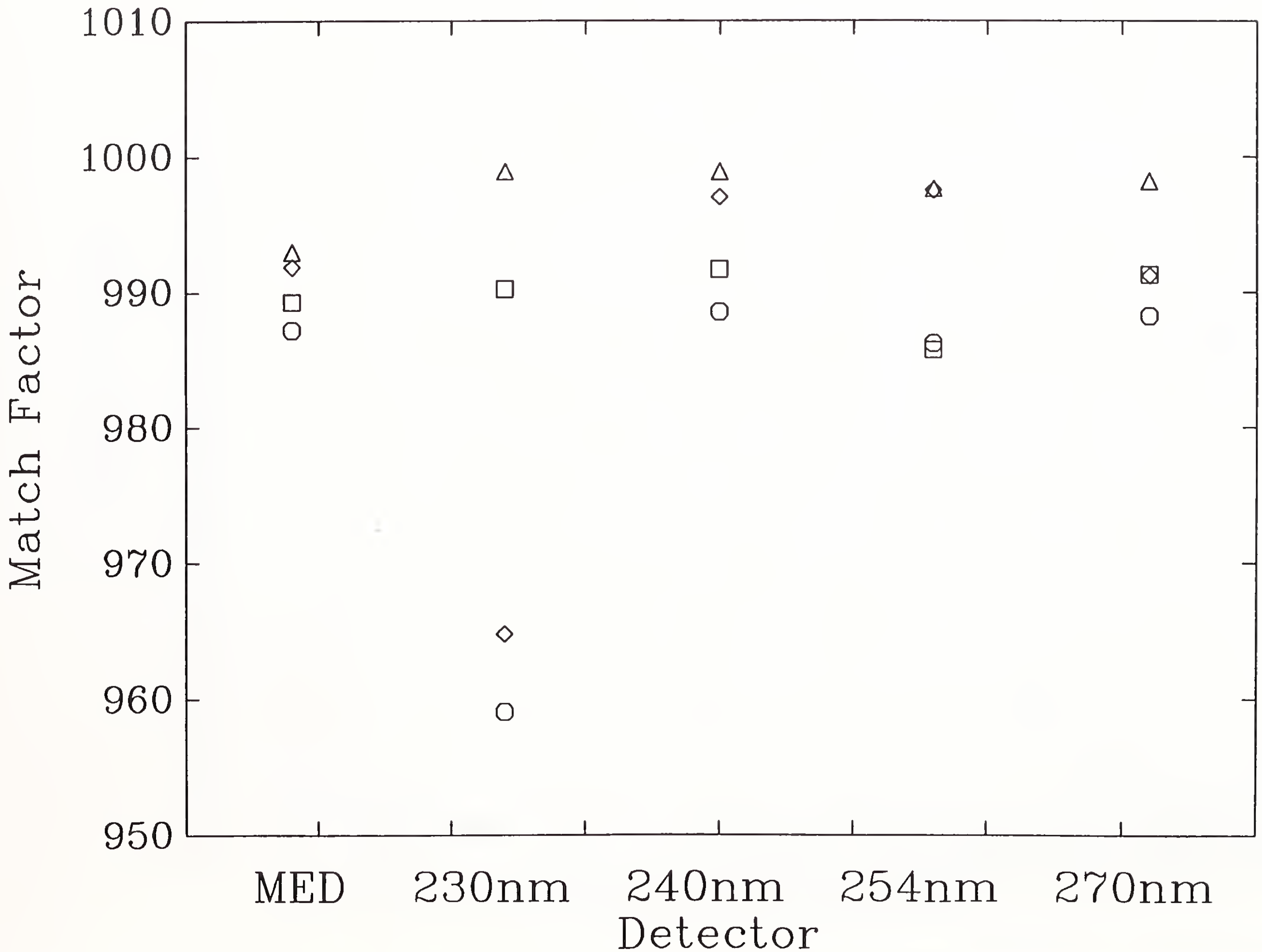


Figure 9. 254 nm UV Response of THF and MEK Extracts

Figure 9a. Matched BHT and MEK

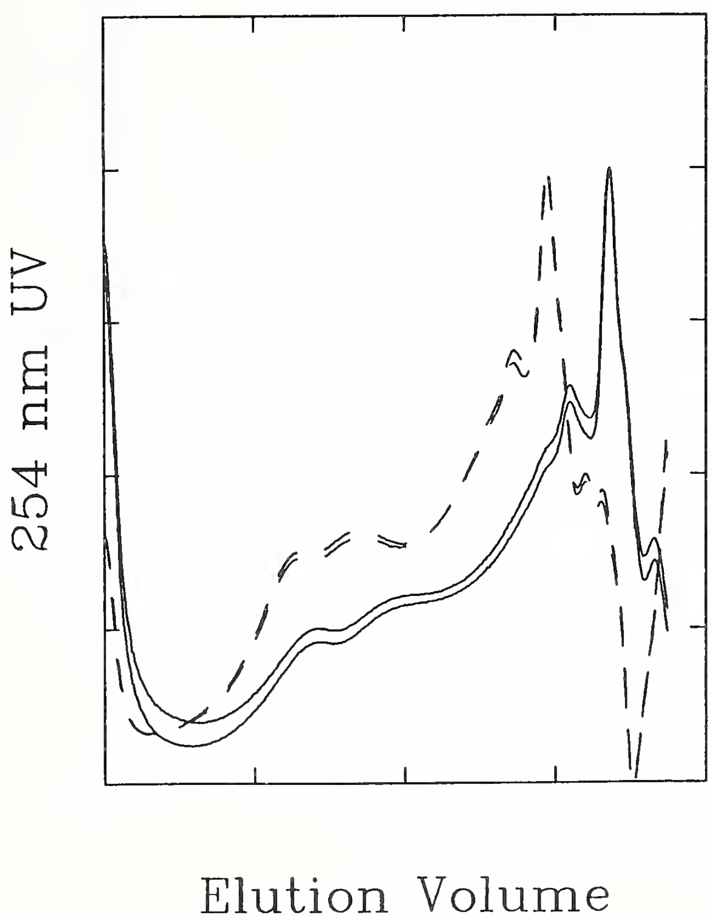


Figure 9b. Matched Main Peak

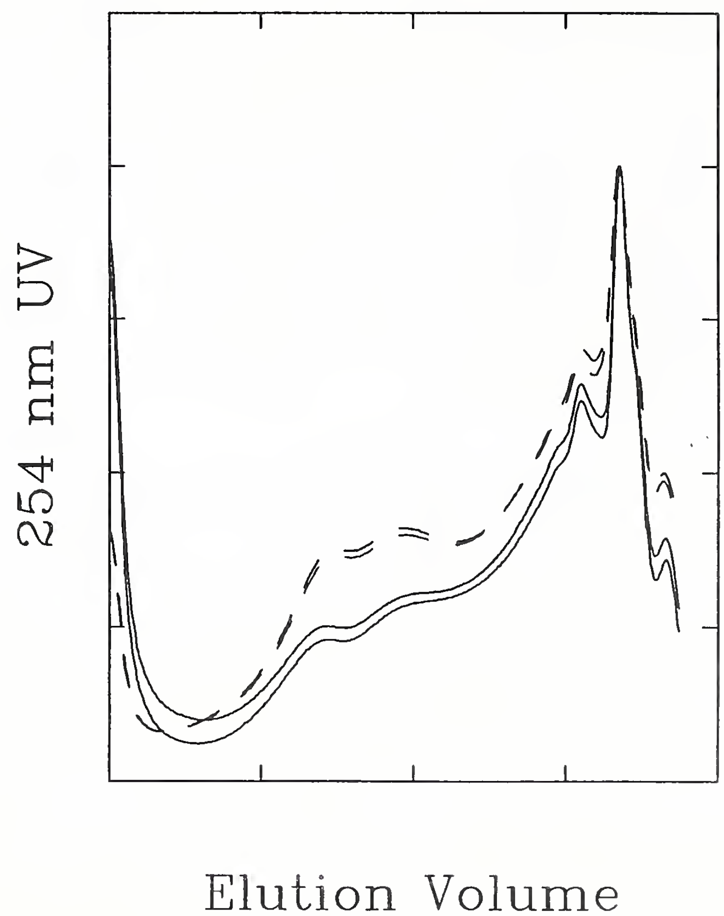


Figure 10. Crumple Numbers and Laundry Numbers

Figure 10a. Black Inks

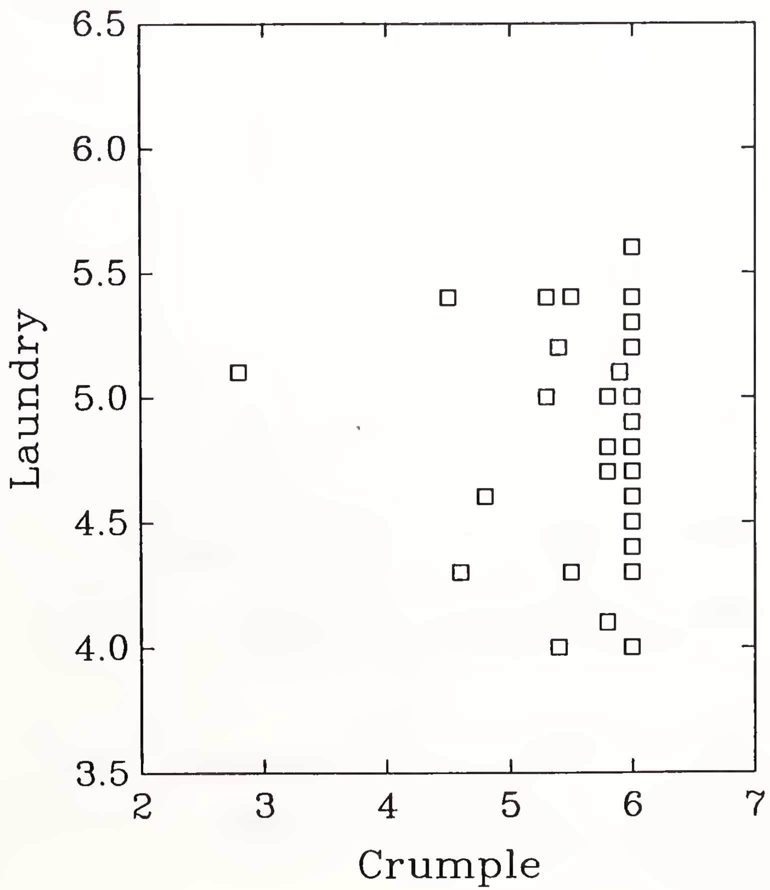


Figure 10b. Green Inks

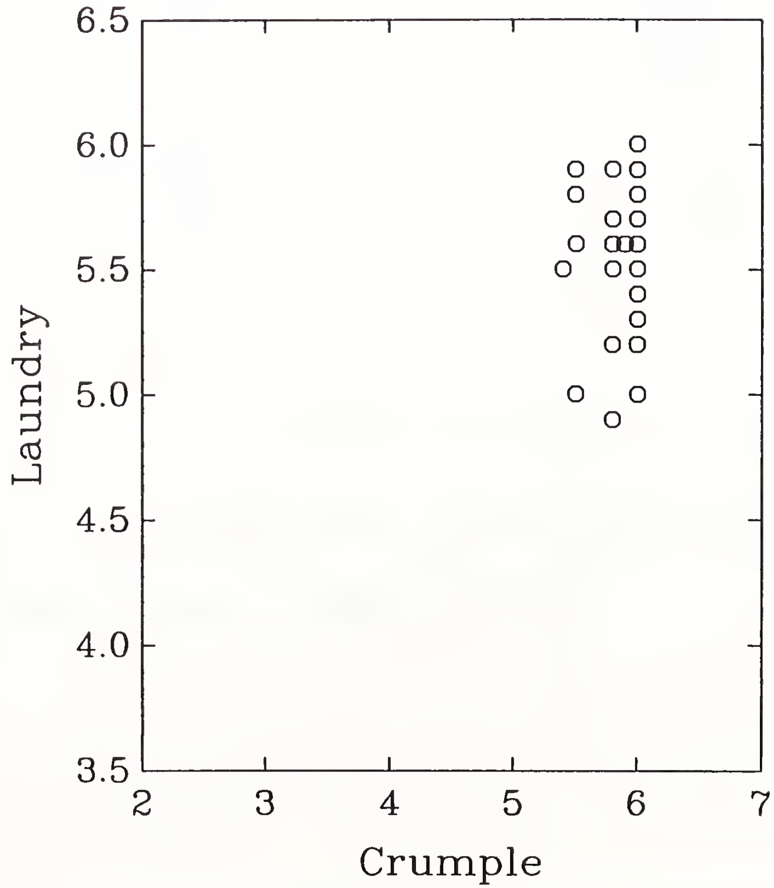


Figure 11. MED Correlations of THF Extracts of Black Inks

Figure 11a. Crumple

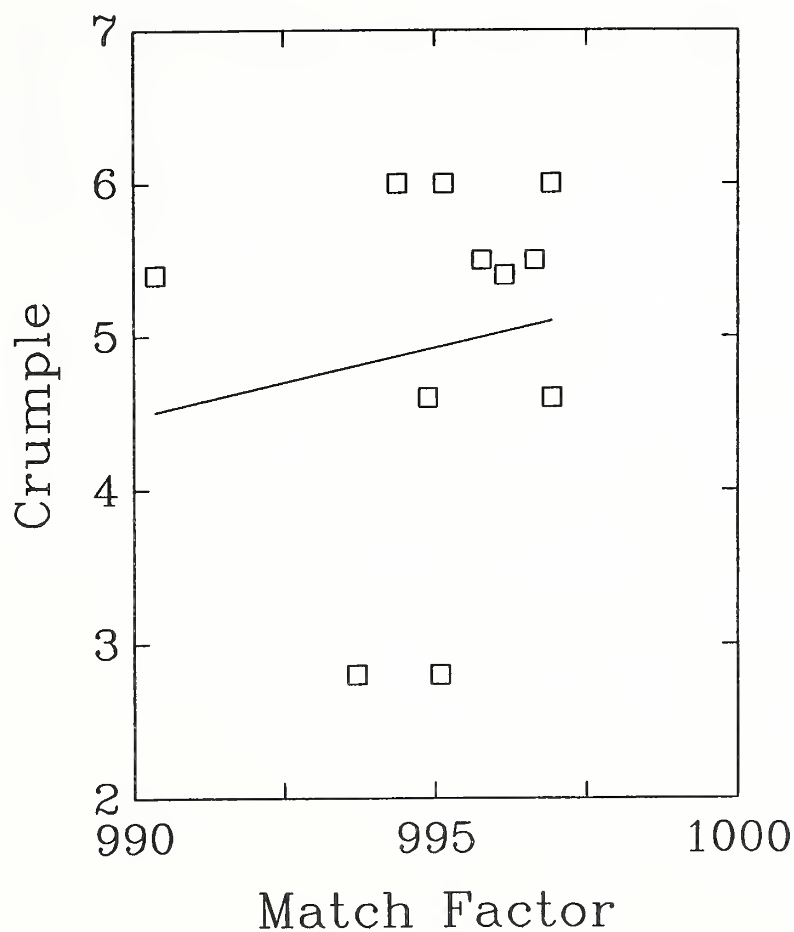


Figure 11b. Laundry

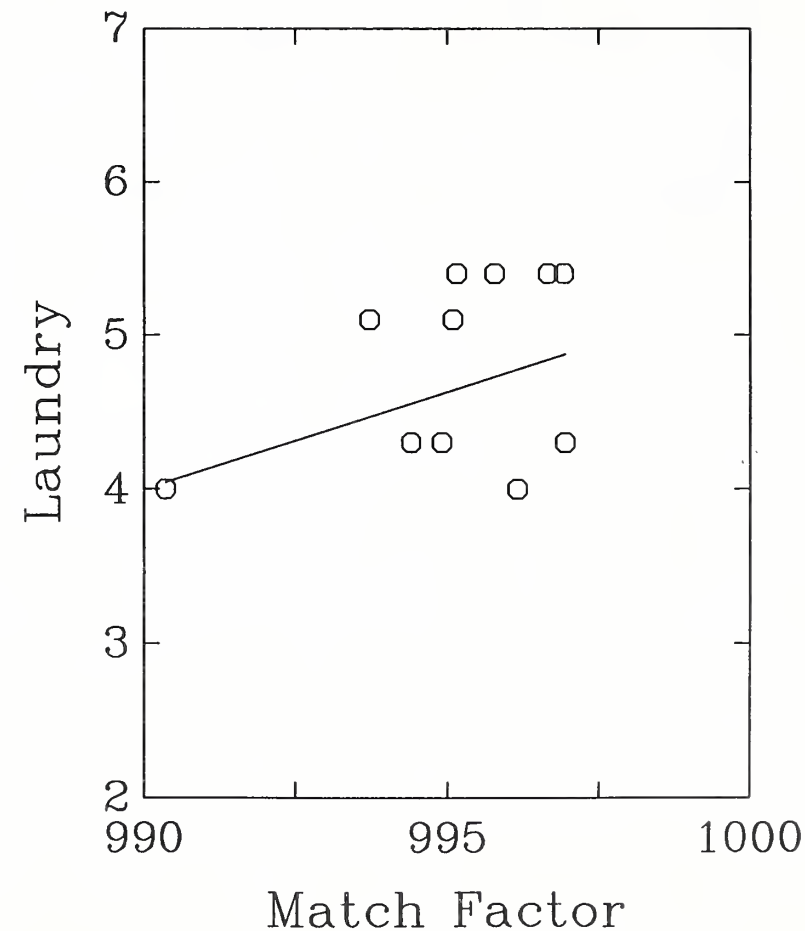


Figure 12. 230 nm UV Correlations of THF Extracts of Black Inks

Figure 12a. Crumple

Figure 12b. Laundry

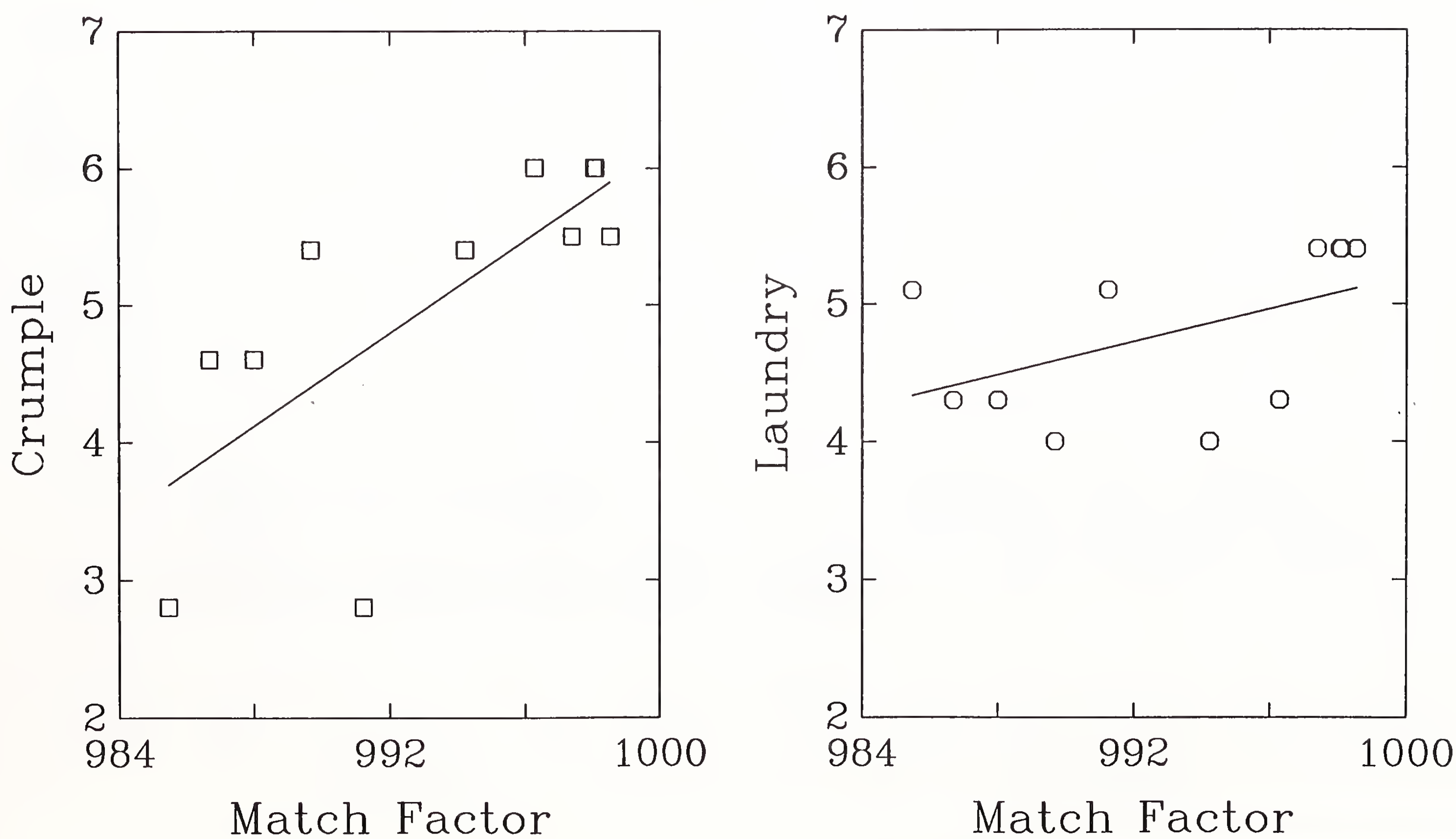


Figure 13. 240 nm UV Correlations of THF Extracts of Black Inks

Figure 13a. Crumple

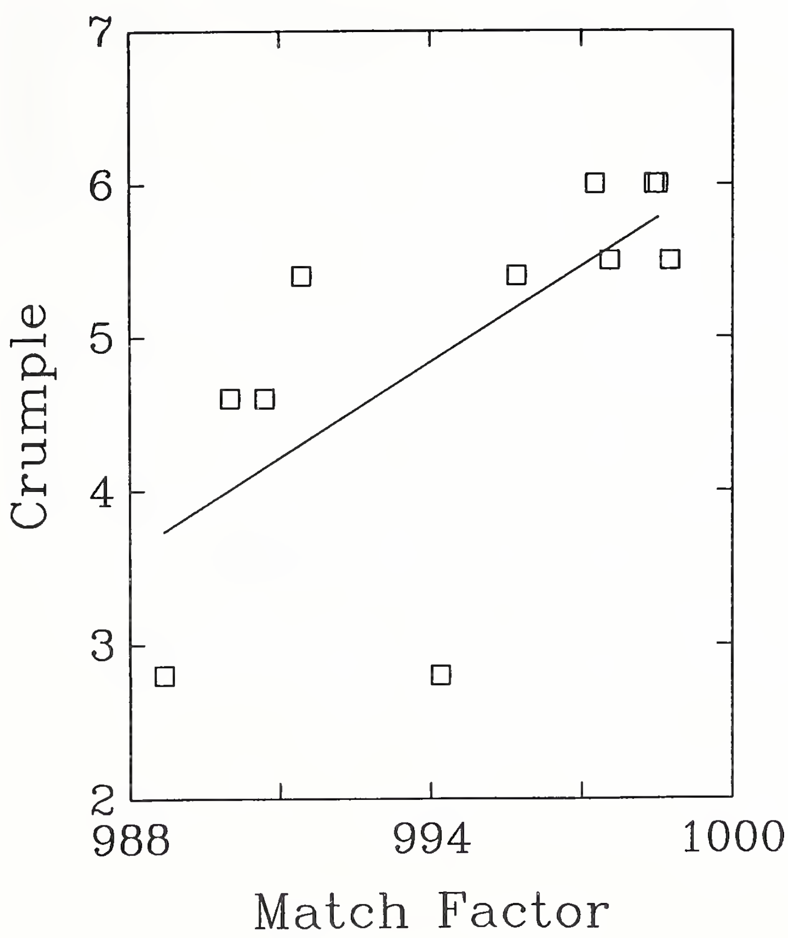


Figure 13b. Laundry

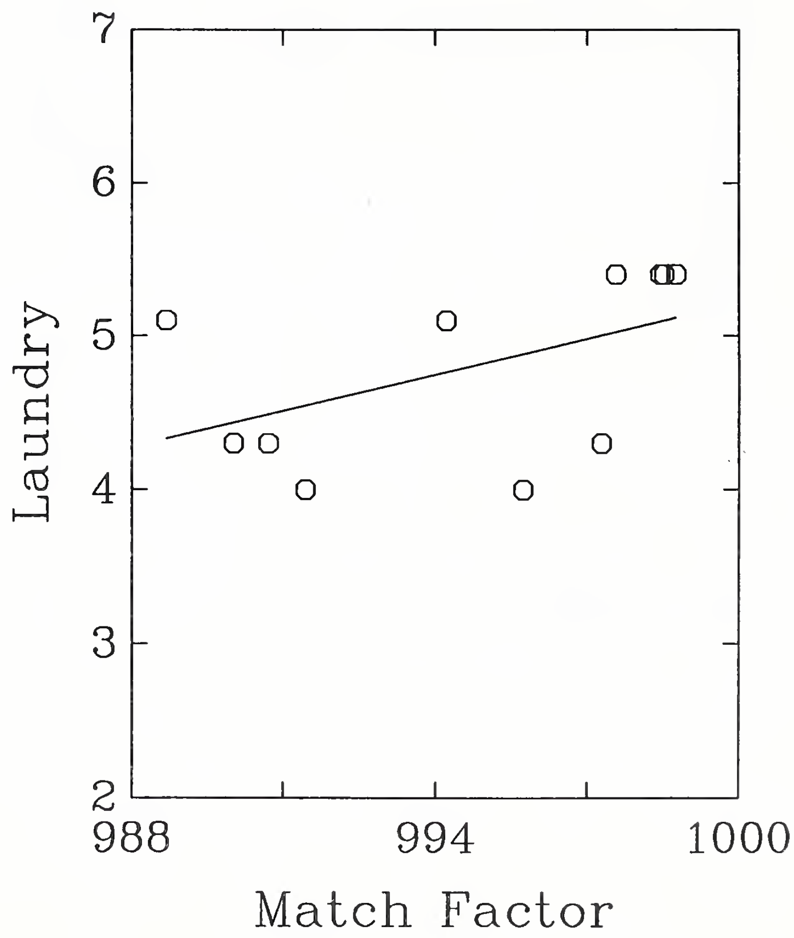


Figure 14. 254 nm UV Correlations of THF Extracts of Black Inks

Figure 14a. Crumple

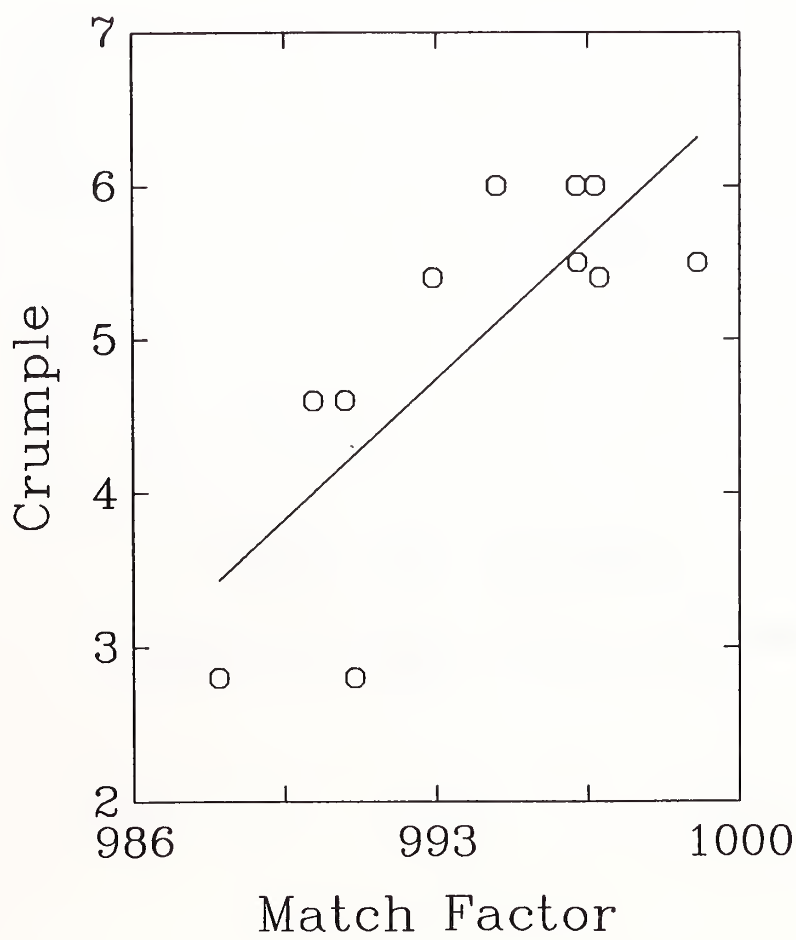


Figure 14b. Laundry

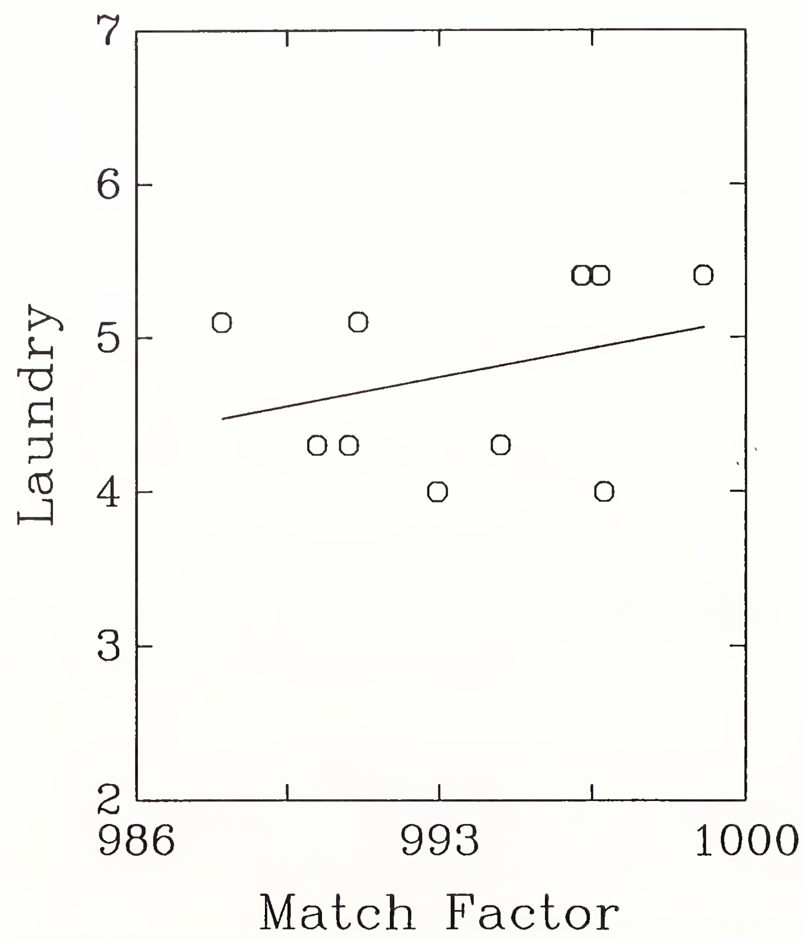


Figure 15. 275 nm UV Correlations of THF Extracts of Black Inks

Figure 15a. Crumple

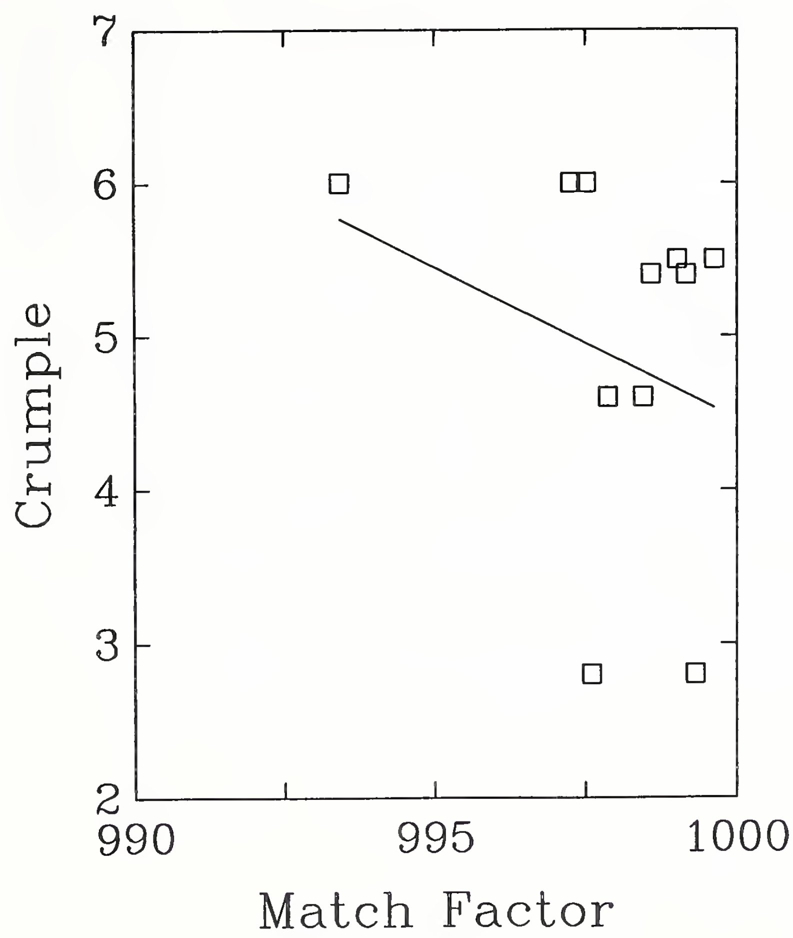


Figure 15b. Laundry

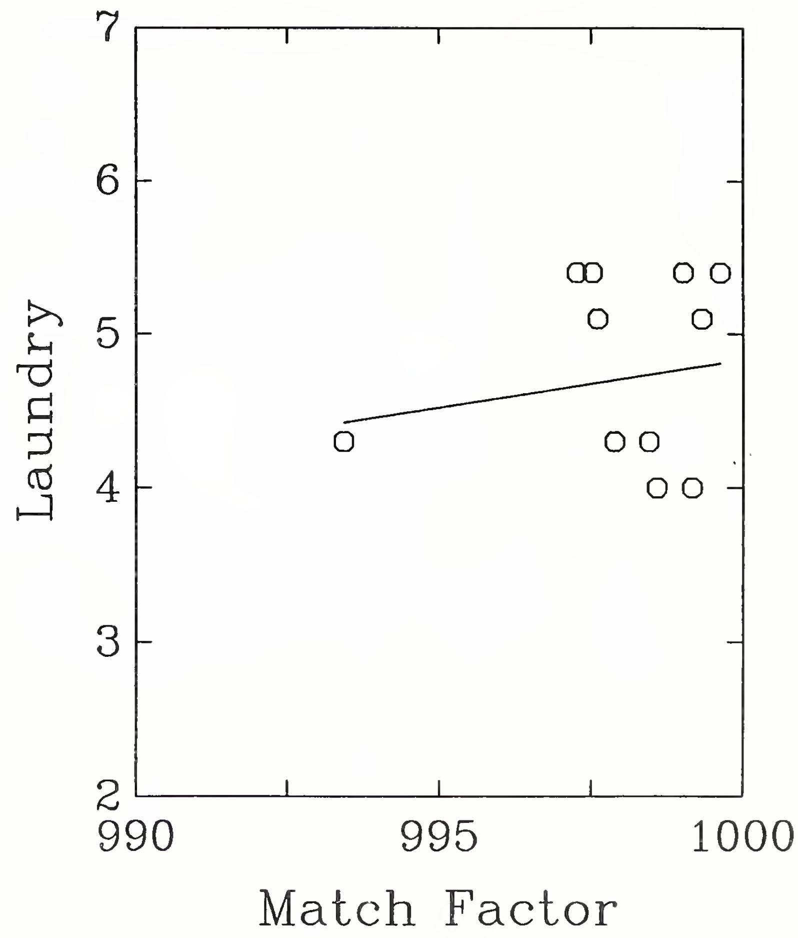


Figure 16. MED Correlations of MEK Extracts of Black Inks

Figure 16a. Crumple

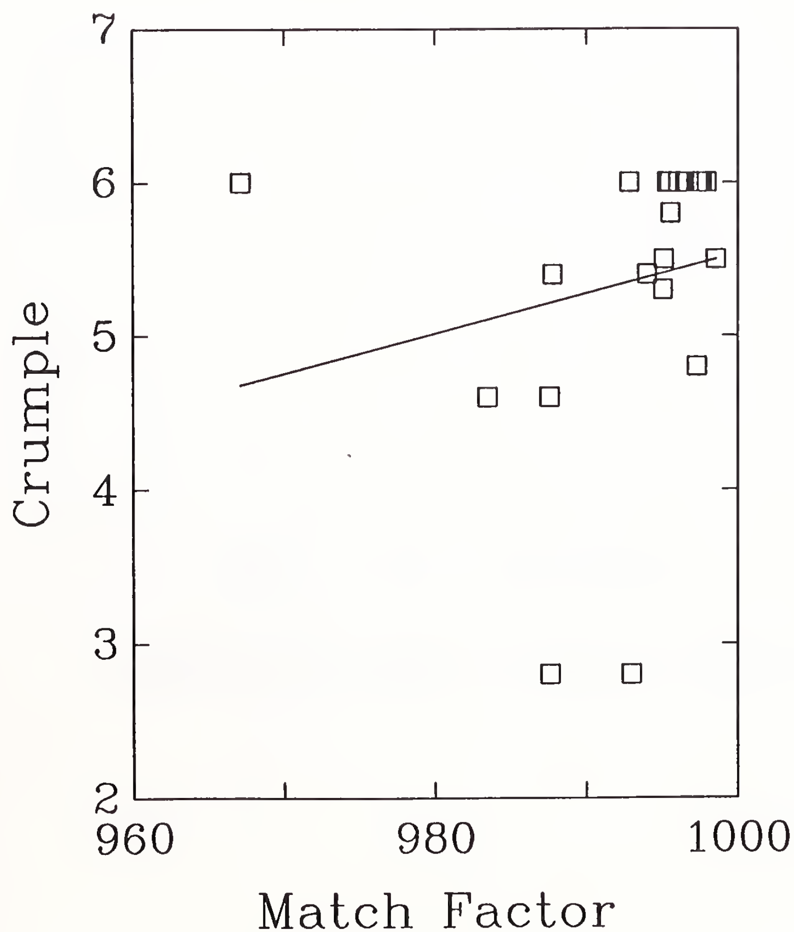


Figure 16b. Laundry

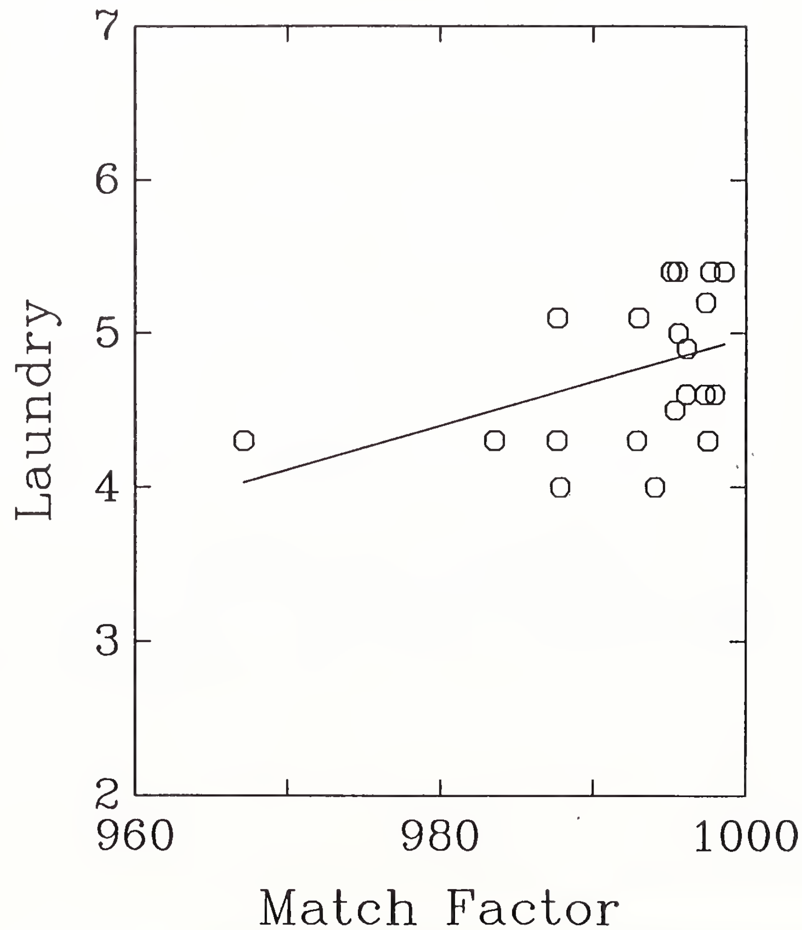


Figure 17. 230 nm UV Correlations of MEK Extracts of Black Inks

Figure 17a. Crumple

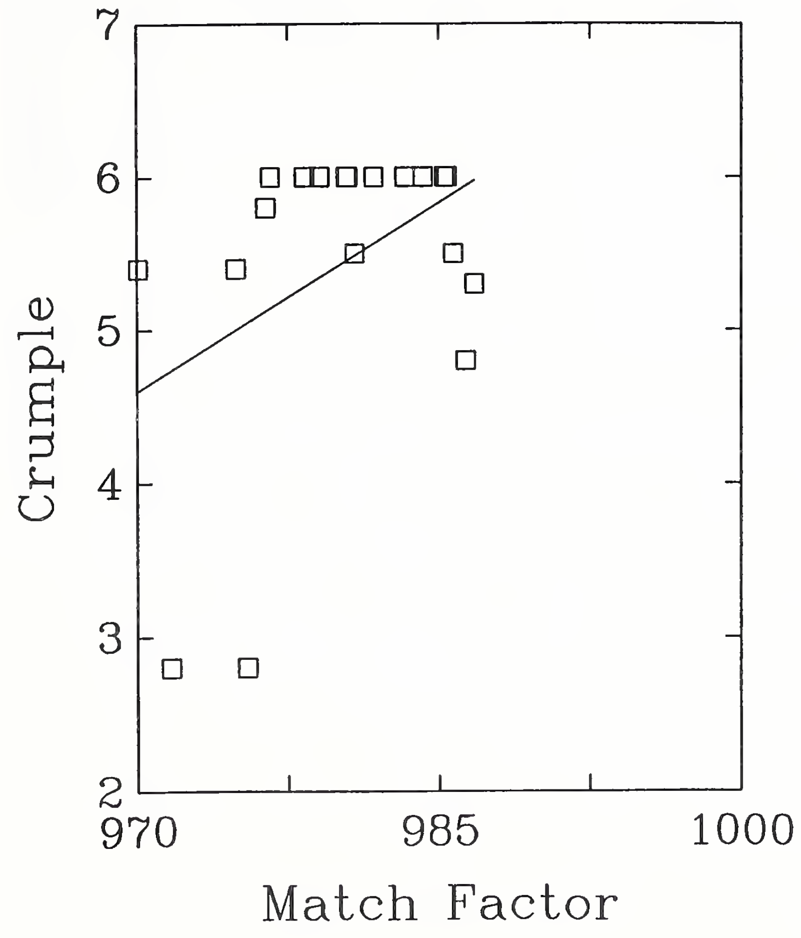


Figure 17b. Laundry

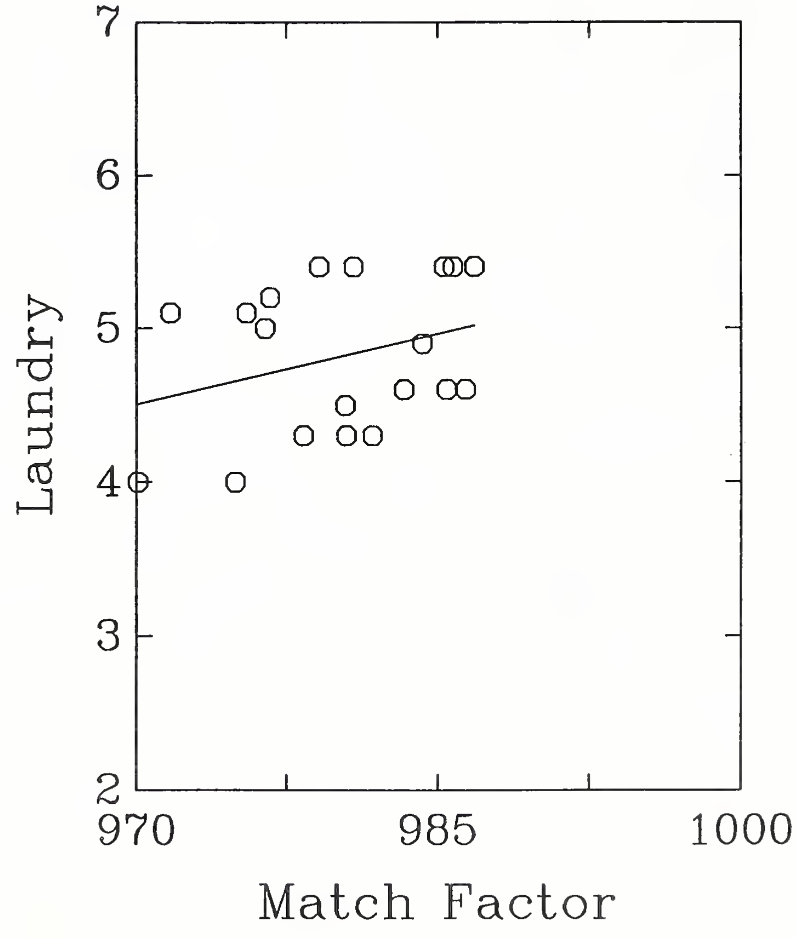


Figure 18. 240 nm UV Correlations of MEK Extracts of Black Inks

Figure 18a. Crumple

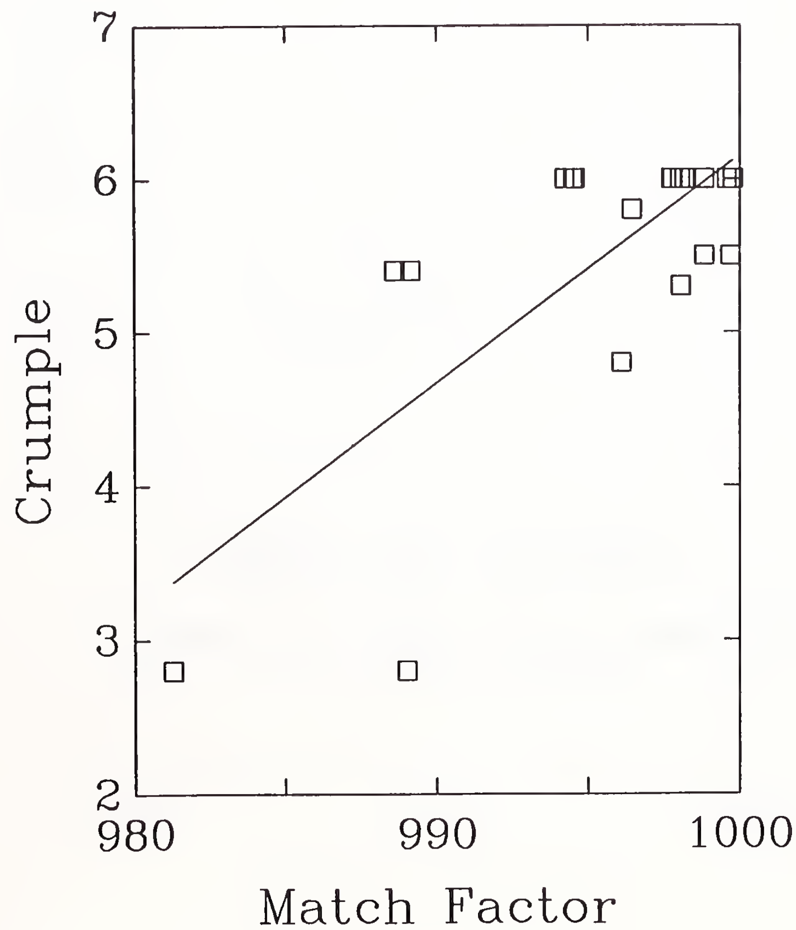


Figure 18b. Laundry

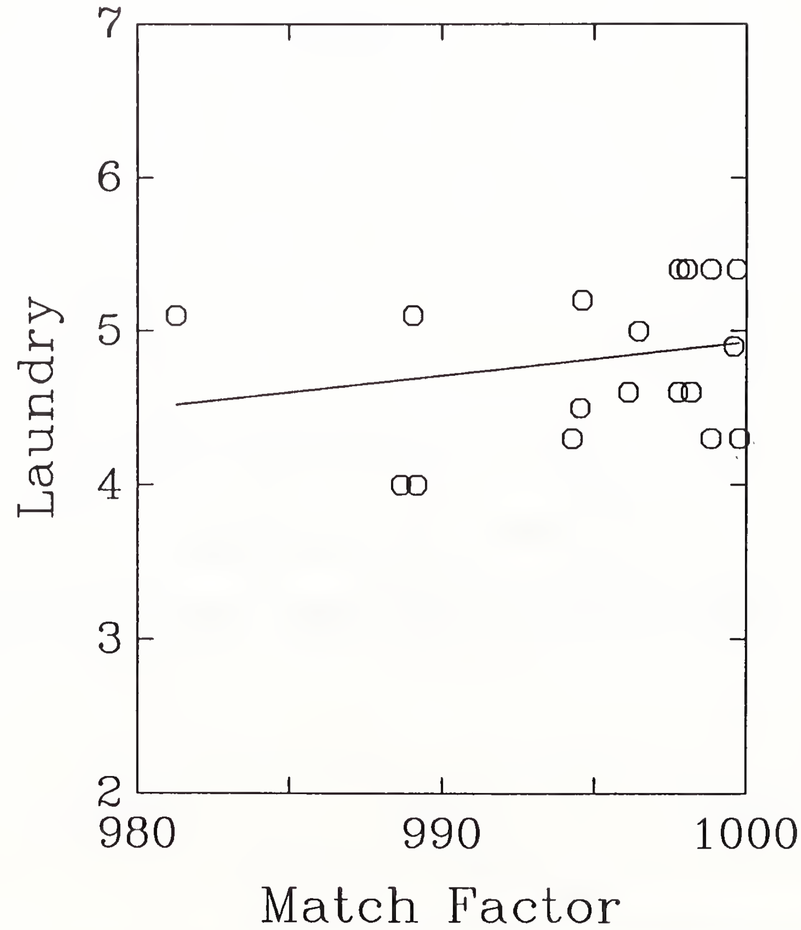


Figure 19. 254 nm UV Correlations of MEK Extracts of Black Inks

Figure 19a. Crumple

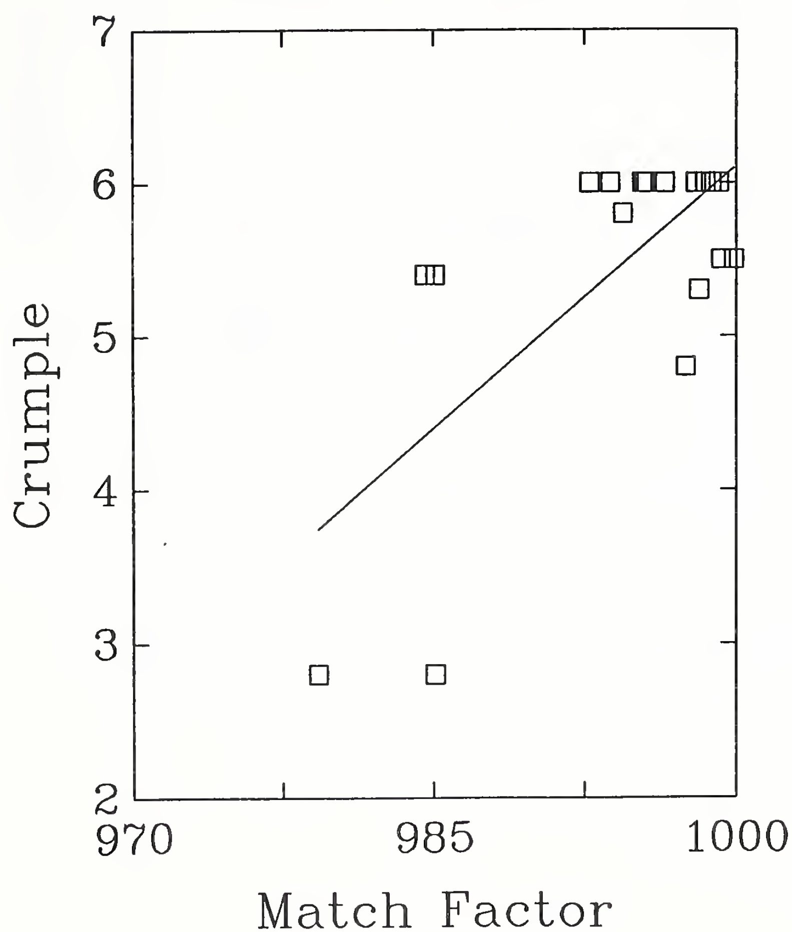


Figure 19b. Laundry

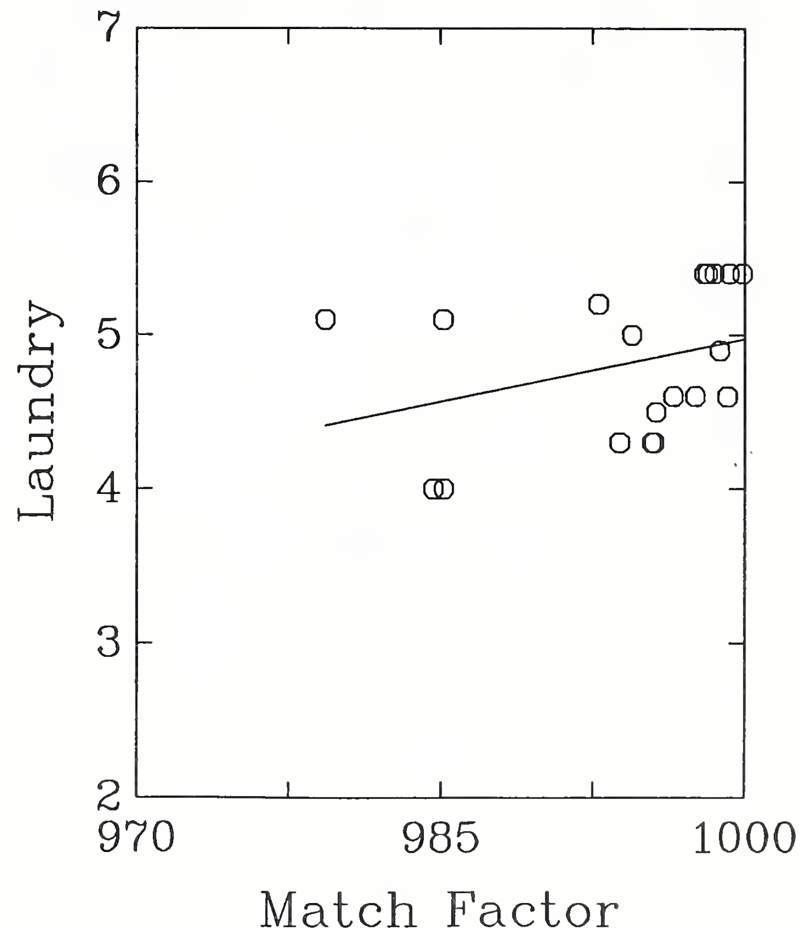


Figure 20. 275 nm UV Correlations of MEK Extracts of Black Inks

Figure 20a. Crumple

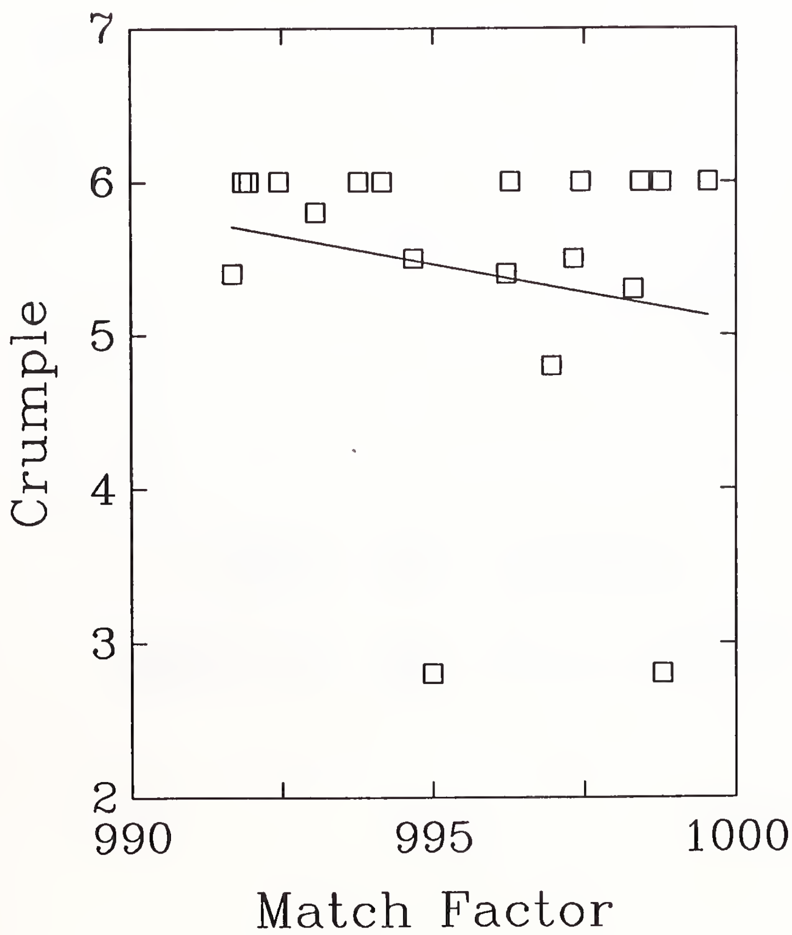


Figure 20b. Laundry

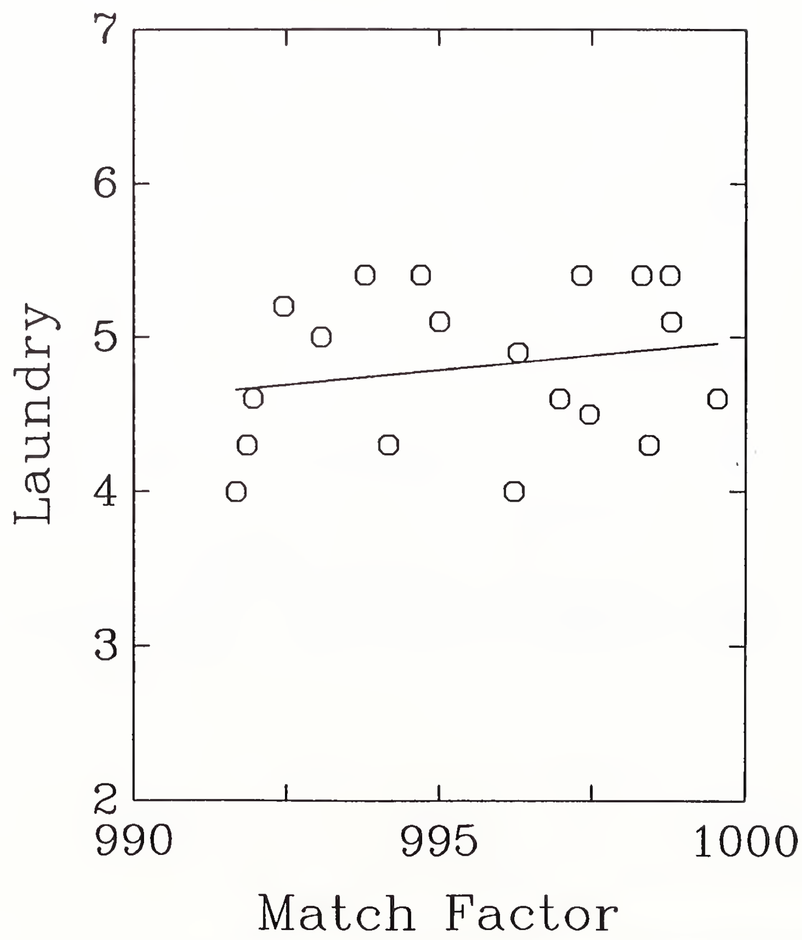


Figure 21. MED Correlations of MEK Extracts of Green Inks

Figure 21a. Crumple

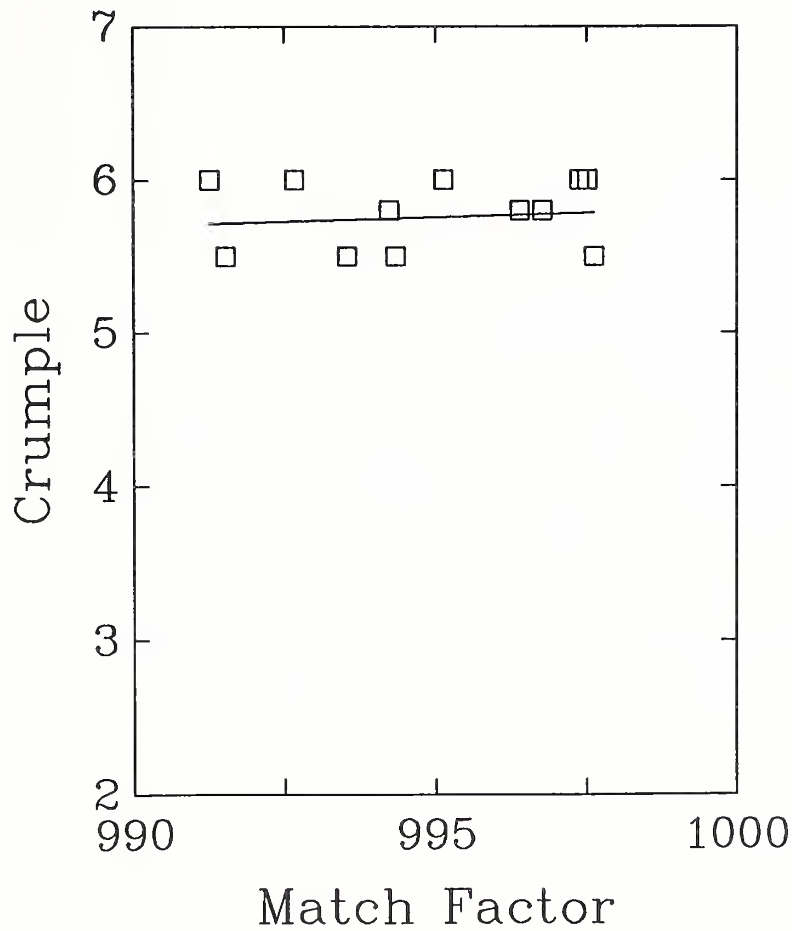


Figure 21b. Laundry

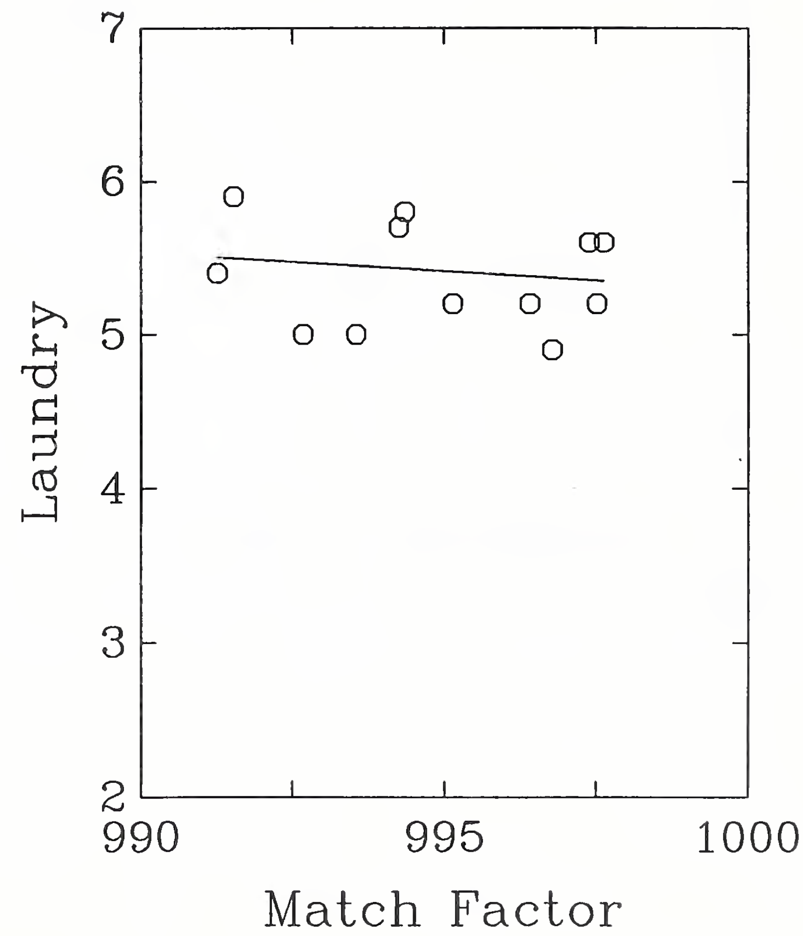


Figure 22. 230 nm UV Correlations of MEK Extracts of Green Inks

Figure 22a. Crumple

Figure 22b. Laundry

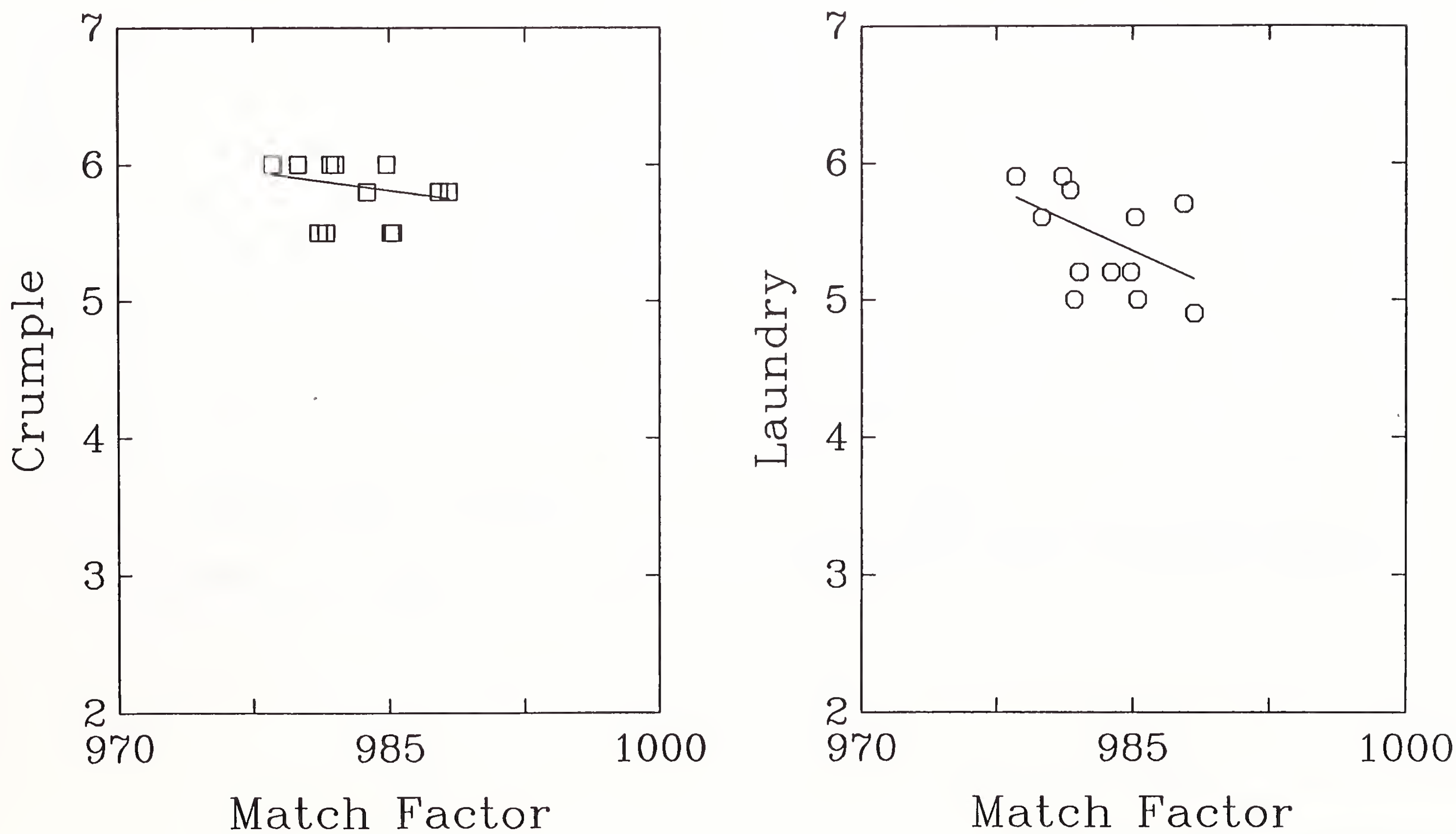


Figure 23. 240 nm UV Correlations of MEK Extracts of Green Inks

Figure 23a. Crumple

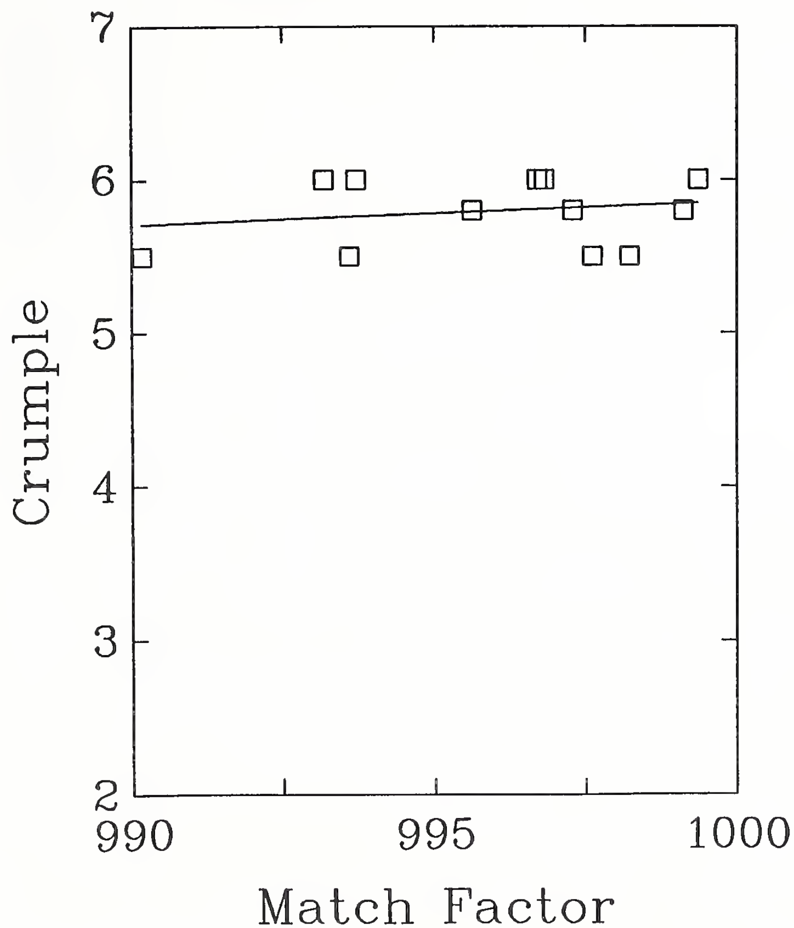


Figure 23b. Laundry

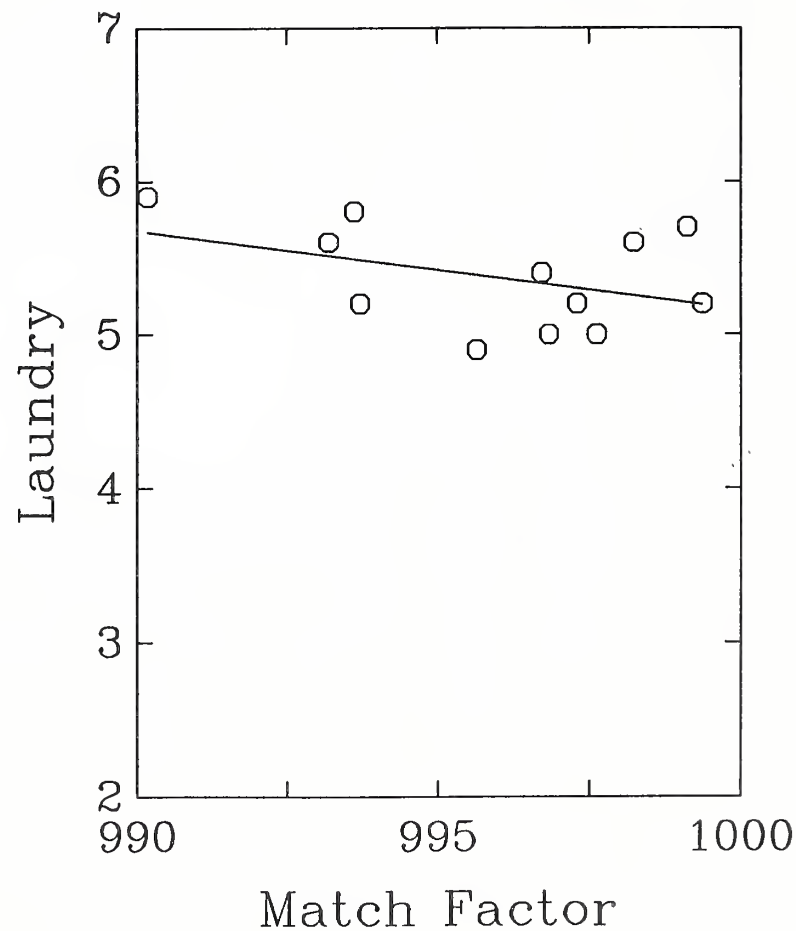


Figure 24. 254 nm UV Correlations of MEK Extracts of Green Inks

Figure 24a. Crumple

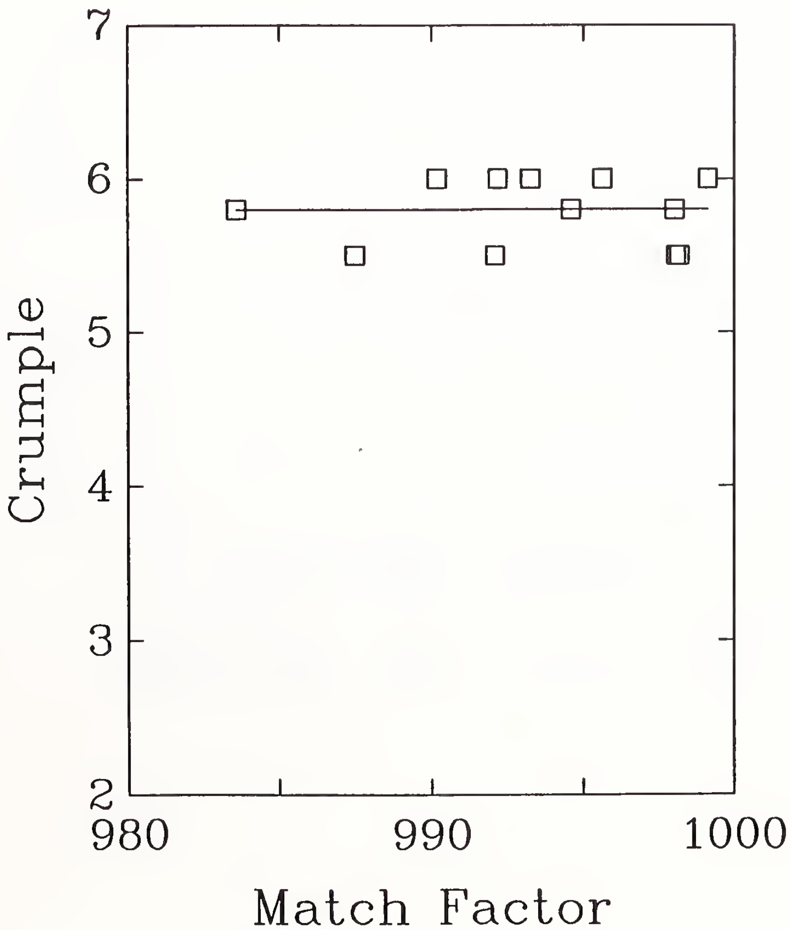


Figure 24b. Laundry

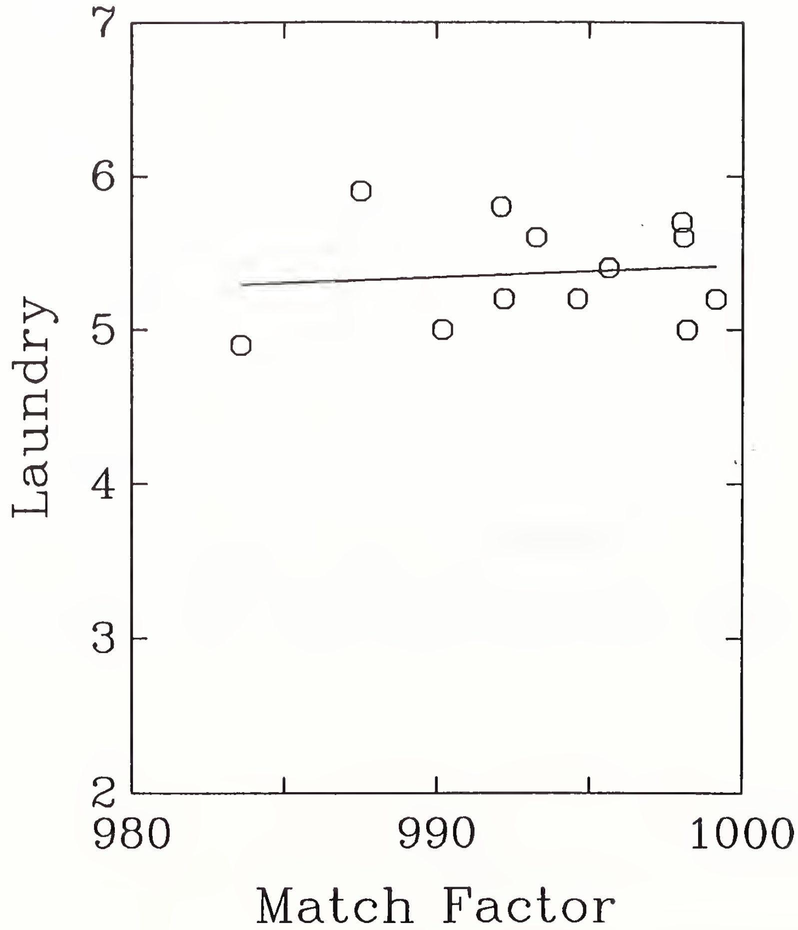
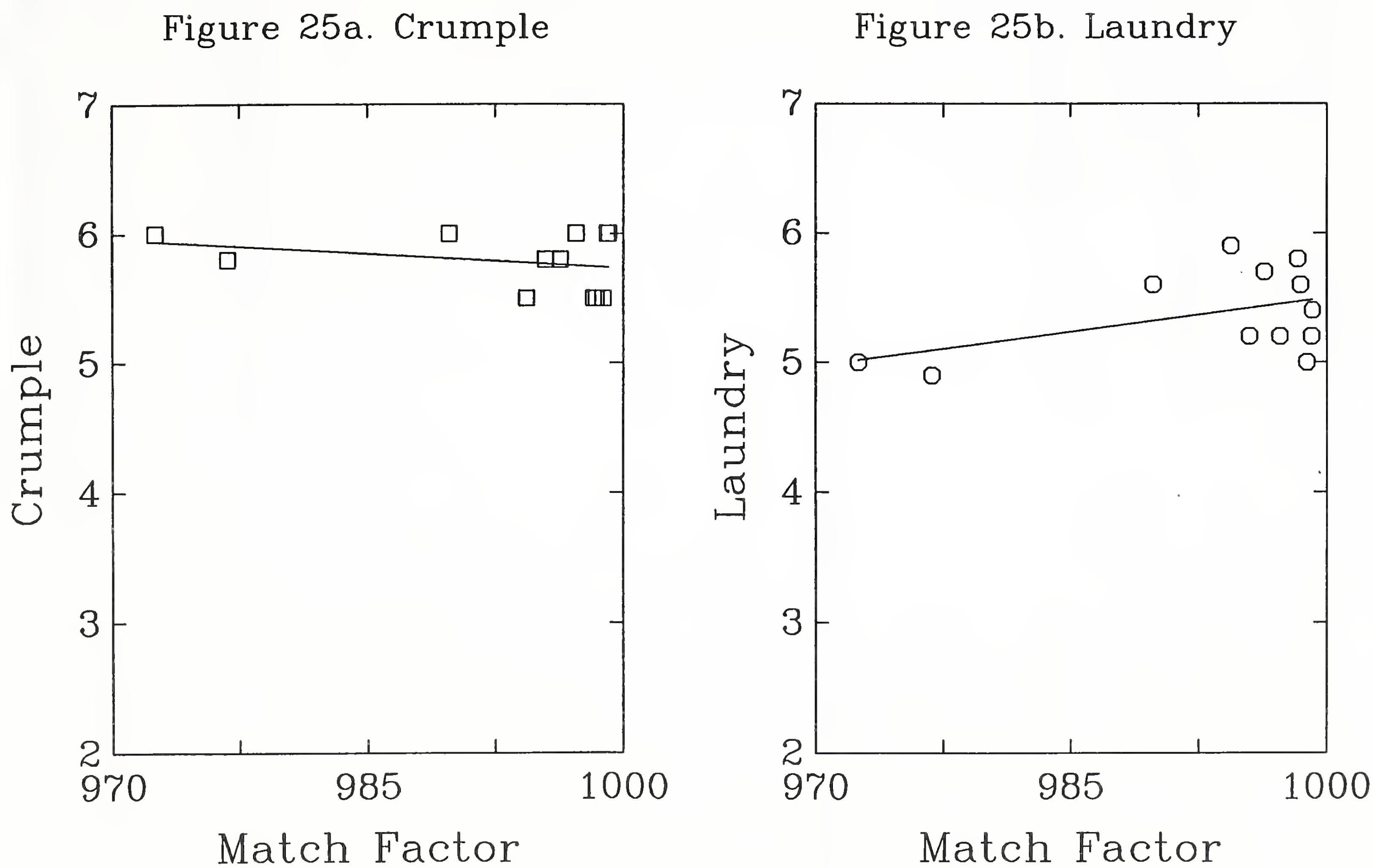


Figure 25. 275 nm UV Correlations of MEK Extracts of Green Inks



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11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

Gel permeation chromatography has been used to characterize inks used in printing U.S. currency. The solvent extractable components of the inks can easily distinguish green and black inks, and differences in ink formulations can be seen. Samples taken from the press match the retain samples well. Poor crumple numbers of inks were correlated to the chromatographic results, but the laundry numbers were not.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

chromatography; crumple; GPC; ink; laundry

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