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A STUDY OF THE INFLUENCE OF IODIDE RELEASED DURING DEVELOPMENT
ON THE COURSE OF DEVELOPMENT

by

Barry J. Britton

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MASTER'S THESIS

by

Barry J. Britton

date

Thesis Committee:

Thesis advisor

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the School of Photographic Arts and Science in the College of Graphic Arts and Photography of the Rochester Institute of Technology

June, 1972

Thesis adviser: Professor Burt H. Carroll

245619

CERTIFICATE OF APPROVAL

MASTER'S THESIS

This is to certify that the Master's Thesis of Barry J. Britton with a major in Photographic Science and Instrumentation has been approved by the Thesis Committee as satisfactory for the thesis requirement for the Master of Science degree.

date

Thesis Committee: _____
Thesis advisor

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A STUDY OF THE INFLUENCE OF IODIDE RELEASED DURING DEVELOPMENT
ON THE COURSE OF DEVELOPMENT

by

Barry J. Britton

An Abstract

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in the School of Photographic Arts and Science in the College of Graphic Arts and Photography of the Rochester Institute of Technology

June, 1972

Thesis advisor: Professor Burt H. Carroll

ABSTRACT

The influence of iodide released during development on the course of development was investigated by transferring known amounts of iodide to Kodak Panatomic X Film and Eastman Fine Grain Release Positive Film (Cine Positive) after exposure and before development. Iodide was transferred to the films being tested by soaking dry Bimat web material in potassium iodide solutions and contacting this to the film for fifteen minutes. The transfer of iodide in the Bimat to the film being tested was found to be essentially complete. The iodide reacted with the grains to convert silver bromide to silver iodide. The silver iodide thus formed appeared to be in a separate silver iodide phase (determined by spectrophotometric analysis) rather than forming a mixed crystal.

Known amounts of iodide were transferred to the test films and developed for various times using DK-50 developer, a developer similar to DK-50 but with a higher pH, and also a hydroquinone developer (H_2Q). Acceleration of Cine Positive development by iodide for the hydroquinone developer was noted for low concentrations of iodide (Lainer Effect). In general, development retardation was observed for the

two Metol-hydroquinone developers. However, Panatomic X developed in hydroquinone showed pronounced retardation for the same amounts of transferred iodide.

Development time series with Cine Positive film were used with DK-50 and H₂Q developers to investigate the influence of the iodide transfer on the induction period and developability of the emulsions. The iodide appeared to shorten the induction period of the hydroquinone developer which could account for the development acceleration (Lainer Effect) which was encountered. The noted acceleration by iodide of Cine Positive film developed in the hydroquinone developer was shown to be true acceleration and not a permanent gain in developability. Retardation of development, however, was shown to increase with prolonged development for both developers, which provides a possible explanation for edge effects which do not disappear with prolonged development.

Abstract approved: _____, thesis adviser
_____, title and department
_____, date

I. INTRODUCTION

Photographic emulsions rarely consist of pure silver bromide grains. Most modern high speed negative emulsions use iodide to form mixed iodobromide grains with improved properties. The amount of iodide used does not normally exceed ten mole percent of the total halide present. Iodide can affect the size, shape, and stress condition of the silver halide grains, it increases the spectral absorption of the emulsion, and it appears to promote chemical sensitization. These facts are well established and familiar to the photographic chemist. However, the role iodide plays during development is a subject about which less is known.

One of the first to focus attention on the role of iodide during development was Lainer.¹ Iodide ions in solution rapidly react with silver bromide or iodobromide emulsion grains; the iodide ions displace bromide ions in the crystal lattice, forming pure silver iodide. This situation is quite different from emulsion precipitation conditions which form mixed iodobromide crystals. Lainer found that by adding a small amount of iodide to some developers, he could effect an acceleration of development.

He added 2cc of a $\frac{1}{4}\%$ solution of iodine to 40cc of oxalate developer, which retarded development and decreased contrast without changing threshold speed. He made no distinction between iodine and iodide, although it is probable that iodine reacted to give iodide in the developer. Iodine caused acceleration of development in a pyro developer and a hydroquinone developer (probably a caustic H₂Q developer), but no acceleration of development was observed for Eikonogen developer.

Lüppo-Cramer² attempted to explain development acceleration of iodide by noting that some silver bromide to silver iodide conversion would occur, and that in the process, the crystal lattice of the silver halide grains would be disrupted or "cracked apart." Thus, internal image would be revealed, and development acceleration could be expected. However, as Stevens discovered for emulsions with sulfur or sulfur plus gold sensitization, "at normal exposure levels, internal image appeared to be formed only in grains which also bore a surface image."³ Lüppo-Cramer's explanation of the "Lainer effect" seems rather forced, as indicated by Sheppard and Meyer,⁴ although he was correct in asserting that the grain disintegrates in the presence of iodide and exposes internal image.

Sheppard and Meyer⁵ explored the effect of soaking an exposed silver bromide emulsion in a dilute solution of potassium iodide before development. Using a hydroquinone

carbonate developer, they observed an acceleration of development by iodide at a low concentration for development times between one and four minutes. They found that one of the effects of the iodide was to reduce the induction period. No such effects with ferrous oxalate as the developer were present. This difference between developers contributed to their rejection of the theory of "keimblosslegung" or "cracking apart" of the grain and caused them to suggest that the formation of silver iodide facilitates adsorption of developing agent to silver halide. Thus, the "revealing" of internal image is not a sufficient explanation for the Lainer Effect.

T. H. James⁶ observed that iodide caused partial conversion of the grain surface to silver iodide and suggested that silver iodide adsorbs hydroquinone and p-hydroxyphenylglycine more strongly than silver bromide. Consistent with the theory that adsorption of a developing agent is a necessary prerequisite to development, this would account for the development acceleration which occurs when a small amount of iodide is added to these developers. Such an explanation of the Lainer Effect is more promising than Lüppo-Cramer's, because it could account for the absence of an effect with some developers and its presence with others. There appears to be little published data on the relative strength of adsorption of developers by silver halides, however. It would seem that further experimentation

to demonstrate the correlation between mole percent iodide, developer adsorption, and development acceleration would be beneficial.

With the exception of the Lainer Effect, the conversion of silver bromide to silver iodide causes the rate of development to decrease because silver iodide is much less readily developed than silver bromide. During development, silver halide is reduced to silver and halide ions are released. The bromide diffuses out into the developer and perhaps plays a minor role in further development, primarily by reducing fog and by affecting AgBr solubility. As noted by Dundon and Ballard,⁷ however, the iodide released from developing grains remains in the emulsion until most of the silver halide is reduced; it therefore must be displacing bromide from the crystal lattice of neighboring grains. This reaction has been shown to be very rapid, and therefore very little escapes out into the developer, at least initially.⁸ An equilibrium is established between iodide used up in the bromide conversion and iodide in solution (the former being greatly favored). As development proceeds toward completion in an area of high developable density, the iodide is first deposited in neighboring areas of less complete development. Eventually, though, the iodide ion must make its way out into the developer as completion of all grain development is approached.

These observations are of considerable importance to the understanding of development processes. Sheppard and Ballard showed that increasing exposure made grains of diminishing size developable,⁹ and Renwick and Sease demonstrated that the larger the grain in one type of emulsion, the higher percentage of iodide it contained.¹⁰ Together, these observations would indicate that more iodide tends to be released per net developed silver in the early period of development, and consequently, more conversion of bromide would be occurring. Consider also the observation that the amount of halide released during development can have a solvent action¹¹ on further development, thereby affecting the ratio of solution-physical to chemical development and covering power while perhaps also revealing internal image. Iodide accumulates in the grains during development so that some of its effects will be greater toward the end of development. Furthermore, its effects will be relatively greater the higher the density. These dynamic roles played by iodide during development hold the key to a better understanding of the subtleties of the development process.

Adjacency Effects

During Dundon and Ballard's investigation of iodide released during development, they realized that "a proper consideration of this mechanism is of great importance in

the interpretation of many development phenomena."¹² It is the apparent lack of consideration of these effects in much of the literature which prompts this research. In addition, it is especially worthy of notice to consider what effect diffusion of iodide across an edge during development would have in influencing or contributing to edge effects for particular developer-film combinations.

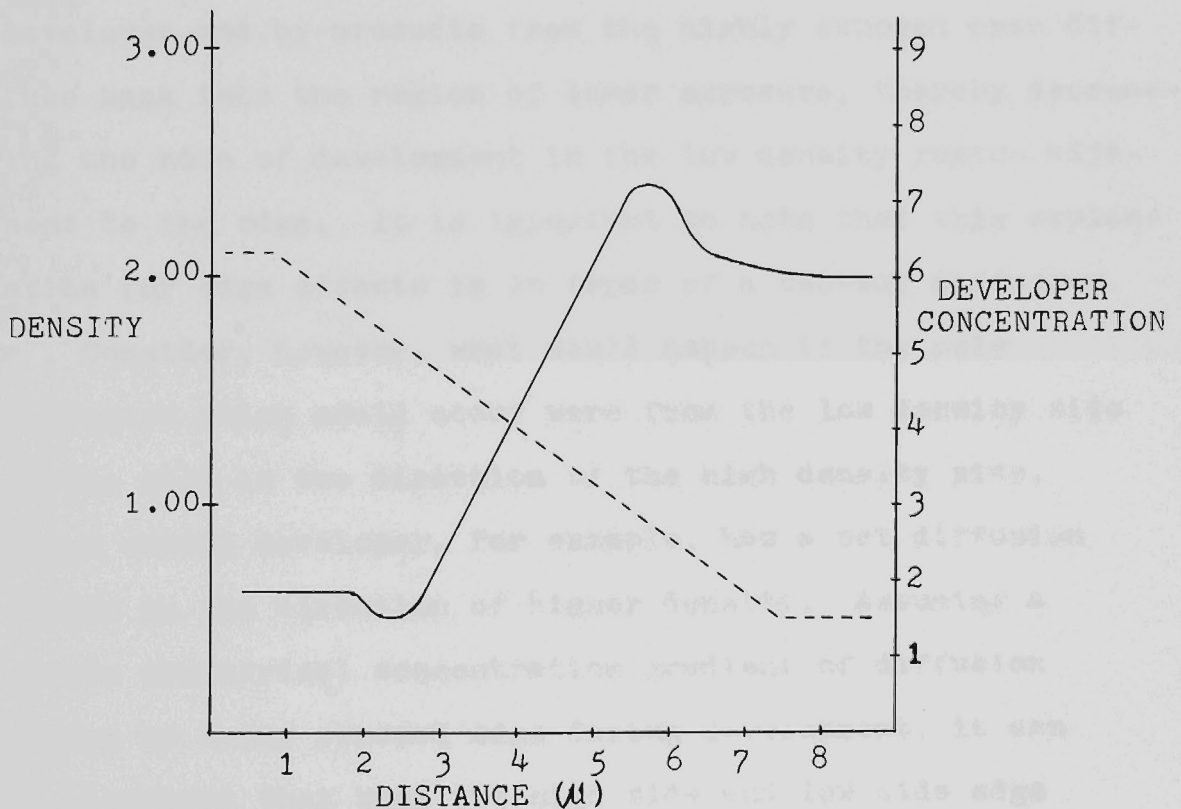


FIGURE 1. This schematic represents a particular instant during the development of a sharp edge exposure. The solid curve describes the developed density as a function of distance and exhibits typical edge effects. The dashed line represents a hypothetical concentration profile (in arbitrary units) of fresh developer as a function of distance across the edge.

The schematic edge trace in Figure 1 demonstrates edge effects one could encounter in microdensitometric measurements. One explanation of this type of effect has been that at the edge boundary, fresh unused developer is diffusing into the adjacent exposed region. This results in a net concentration adjacent to the edge which is higher than at a distance from the edge where exhaustion and therefore depression of density is occurring. Conversely, exhausted developer and by-products from the highly exposed area diffuse back into the region of lower exposure, thereby decreasing the rate of development in the low density region adjacent to the edge. It is important to note that this explanation for edge effects is in terms of a two-way diffusion.

Consider, however, what would happen if the only diffusion which could occur were from the low density side of the edge in the direction of the high density side. Fresh unused developer, for example, has a net diffusion vector in the direction of higher density. Assuming a simple symmetrical concentration gradient of diffusion across an X-ray exposed edge during development, it can be theorized that both the high side and low side edge effects are partially accounted for by the gradient.

It is best to consider both sides of the physical edge in Figure 1 separately. On the high density side of the actual physical edge and adjacent to the edge, a higher concentration of fresh developer is found than at

a distance from the edge. Nelson¹³ observed that the enhancement of density at the edge (border effect) is not acceleration, but rather that the lower density at a distance from the edge is due to retardation. In this case, the relatively lower concentration of developer at a distance from the edge would result in a reduced rate of development as compared to the border effect area where more fresh developer is available. The explanation of the border effect is similar to that for observed increases in maximum density for progressively narrower lines.¹⁴

Similarly, the conditions on the low density side of the physical edge in Figure 1 can be analyzed by noting that the concentration of fresh developer at a distance from the edge is higher than the concentration adjacent to the edge. This would account for the relative depression of density adjacent to the edge (fringe effect). The fringe effect occurs in a region of lower densities so its effect is smaller than the border effect.

In this manner, a consideration of net diffusion of fresh developer in one direction can be assigned as one possible factor in creating both edge effects. A little reflection will show that any one retarder or accelerator of development which has a net diffusion profile across the edge similar to or in reverse to that of the fresh developing agent can act in a like manner in influencing

border effects. Fresh developer, exhausted developer, halide ions, and hydrogen ions can be included as factors in this hypothetical explanation of edge effects. The relative contributions of these sources responsible for edge effects do not seem to be well documented. The role of hydrogen ion is not normally mentioned in connection with edge effects, although hydrogen ion has a definite influence on developer activity. One source, or more likely, a combination of these sources could be an explanation for edge effects.

This analysis might be academic if it were not for the need to avoid oversimplification which could obscure clear analysis of the possibilities. For the purposes of this paper, these considerations are important because the subject of concern here is the diffusion of iodide ions which is essentially a diffusion in one direction (from high concentration area to low concentration area).

Similar to the discussion in connection with developer and developer by-product diffusion in a single direction, diffusion of iodide ion in one direction could hypothetically create or enhance both edge effects as diagrammed in Figure 1. These observations, of course, are hypothetical because the shape of the concentration gradients are not known (for example, it is not known how the width of the concentration gradients as a function of time compares to the width of the optical spread function of a particular

film type). Nevertheless, this model points out the fact that although the iodide diffuses in only one direction, it could have a contributing effect in creating edge effects on both the high and low density sides of the edge.

A complete analysis of this model would have to account for the shape of the concentration profile across the edge as a function of time. No experimental results are shown here to test the validity of this model. The justification for presenting it rests on the observation that current discussions of edge effects in the literature^{15,16,17} do not go far enough in analyzing the consequences of diffusion of retarders and accelerators across a developing edge.

As indicated, some work has been accomplished in the past with addition of iodide to developers. This technique is inherently limited by its inability to state results in terms of the amounts of iodide involved. When iodide is added to the developer, conversion of silver bromide to silver iodide and development must occur simultaneously. Thus, the relative rates of the two reactions are of considerable importance in analyzing results.

It was decided that it would be beneficial to transfer known amounts of iodide to exposed films and then develop them with different developers and development conditions to determine the influence of iodide on development. In

particular, it was desired to observe the influence of iodide on development retardation and acceleration, relative induction periods, relative speed, and contrast index.

The edge effects which are produced by the diffusion of retarders and accelerators across a developing edge should, in general, disappear with prolonged development as completion of development is approached. In practice, edge effects are decreased, but by no means disappear.¹⁸ It was suspected by Dr. B. H. Carroll¹⁹ that part of the explanation for the lack of complete disappearance of edge effects could be a permanent retardation of development by iodide. One of the primary objectives of this research was to prove or disprove this hypothesis.

II. PRELIMINARY EXPERIMENTS

Iodide Transfer Technique

The purpose of this research was to gain insight into the effect on development of iodide liberated during development. Because iodide also plays a role in sensitizing photographic emulsions to light, it was first necessary to develop a technique which would enable isolation of the role of iodide released during development from its other roles. It is practical consideration that varying the amount of iodide in the original emulsion would complicate matters by confounding the effect of iodide liberated during development with its other effects, for example, on crystal structure and chemical sensitization.

A method was proposed by Dr. B. H. Carroll²⁰ in which Bimat Transfer Film (consisting of only gelatin on a film base) is used to transfer a known amount of potassium iodide to the exposed negative film being tested. The dry Bimat material is soaked for a predetermined length of time in a solution of potassium iodide having a concentration such that the desired amount of potassium iodide per unit area is absorbed. Then, the Bimat is cleared of surface droplets and placed in intimate contact with the exposed negative emulsion and allowed to remain

in contact until completion of transfer is accomplished. It was anticipated that the transfer of iodide would be nearly complete because of the conversion of silver bromide to silver iodide. Subsequently, the film is processed and the change in the development response of the film is analyzed.

Having decided on a general technique of iodide transfer, it was also necessary to find the best method of implementing the transfer technique and to choose the proper films, developers, and development conditions to demonstrate the role of iodide released during development. The investigations included spectrophotometric analysis of film with different amounts of iodide transferred to it, the determination of the degree of completion of transfer of the iodide to the negative emulsion, and silver analysis to determine coating weight of the film types chosen.

Developers

An important consideration in the experiments performed was the choice of developing agents and developer formulations. Sheppard and Meyer²¹ in their experimental observations of the Lainer Effect used a hydroquinone carbonate developer. They also indicated that iodide can accelerate development by hydroquinone developers, but can only decrease the rate of development with Metol as the developing agent. Consequently, a hydroquinone (H_2Q) and

a Metol-hydroquinone (MQ) developer were used as two representative types of developers. The hydroquinone developer (H₂Q) was a modified version of the DK-50 formulation in which an equimolar amount of hydroquinone replaced the Metol normally found in DK-50 developer.

Table 1. Developer formulations in grams per liter. Sodium hydroxide amounts are approximate (NaOH was added to the developer solution as a unit normal solution until the desired pH value was attained).

	DK-50 (pH=9.58)	H ₂ Q (pH=10.60)	DK-50* (pH=10.67)
sulphite	30.	50.	50.0
Metol	2.5		2.5
hydroquinone	2.5	6.4095	2.5
Kodalk	10.0	10.00	10.0
KBr	.5	2.50	2.5
NaOH		1.88	1.88

As indicated in Table 1, the H₂Q developer had other modifications of the basic DK-50 formulation. Before raising the pH, the H₂Q developer had insufficient activity to be used at practical development times. Hence, the pH of the H₂Q developer was adjusted by additions of sodium hydroxide to give it a pH of approximately 10.60. At a later time it was decided to use a third developer, DK-50* which had a pH comparable to that of the H₂Q developer (and a higher activity). This was considered desirable in order to determine if observed differences in the results obtained with H₂Q and DK-50 developers were due to the disparity between

their pH levels, or if they were due to other properties of the developers. The formulations of the three developers are found in Table 1.

Agitation

Preliminary work with the Kodak Model 11 Color Drum Processor indicated that it gave very consistent agitation. Some of its disadvantages were the tendency to produce a density gradient the length of the film (directional effects), the difficulty of cleaning the mounting net adequately between runs, and the limitation to five 35mm strips per experimental run. Mounting and removing test strips in total darkness were also difficult at times.

Therefore, it was decided to investigate the feasibility of using nitrogen burst tank agitation. An experimental model constructed by Mr. Richard Norman²² was available at Rochester Institute of Technology (the design and statistical evaluations are to be found in Appendix C). Statistical evaluation of the eight-well nitrogen burst tank (a "well" is one of eight positions for test strips within the nitrogen burst tank) for one set of exposure and development parameters indicated negligible directional effects, and an F-test of the mean square due to wells against the residual mean square was not significant for an alpha risk²³ of .05. The standard deviation (calculated from the mean square

due to wells only) versus density is plotted below.

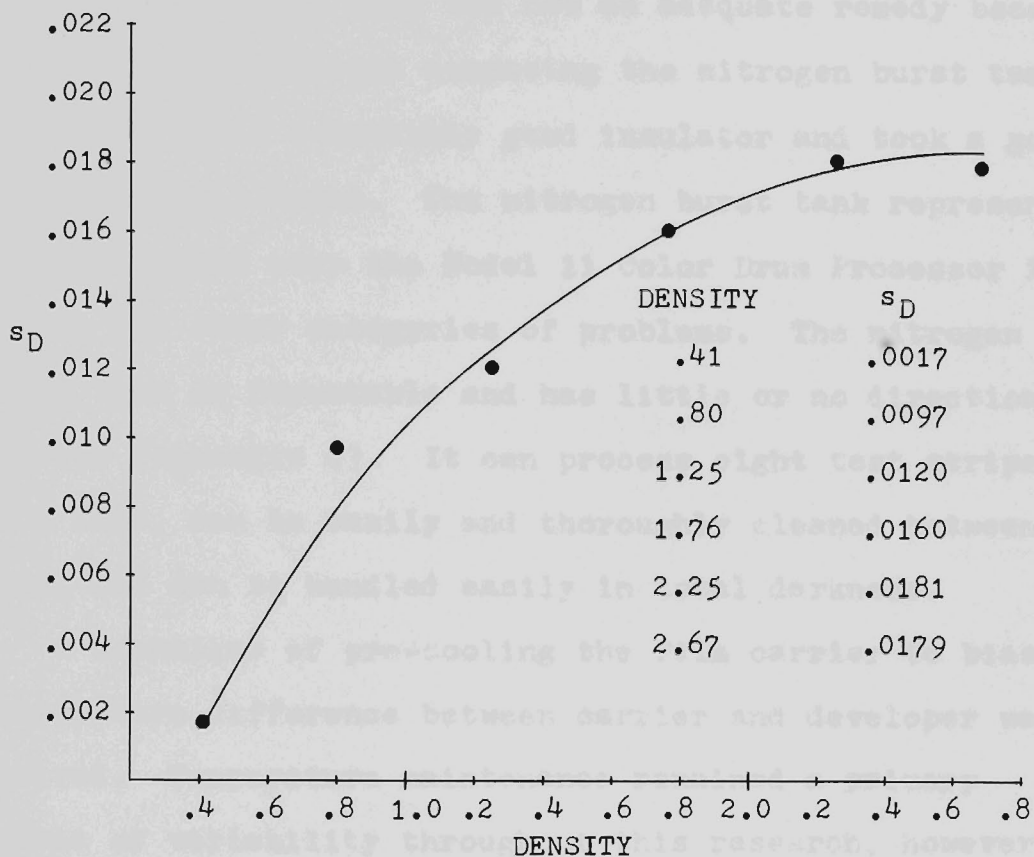


FIGURE 2. The standard deviation due to wells, only, versus density for six development runs and eight Cine Positive test strips per run (Appendix C).

In all cases, however, the mean square due to runs was significant, and it was apparent that considerable care would be required to lower the variability due to runs. It became apparent as the research proceeded that constant development temperature was one of the most strict requirements for reproducibility. The introduction of the film carrier which was in equilibrium with ambient air

temperature into the developer brought about a change in temperature of the developer. A simple water bath around the nitrogen burst tank was not an adequate remedy because the Plexiglas material composing the nitrogen burst tank apparatus was a relatively good insulator and took a good while to equilibrate. The nitrogen burst tank represents an improvement over the Model 11 Color Drum Processor in almost all other categories of problems. The nitrogen burst tank is repeatable and has little or no directional effects (Appendix C). It can process eight test strips at a time, can be easily and thoroughly cleaned between runs, and can be handled easily in total darkness.

A technique of pre-cooling the film carrier to bias the temperature difference between carrier and developer was derived. Temperature maintenance remained a primary source of variability throughout this research, however.

Quantitative Iodide Analysis

One of the primary objectives of this research was to determine the quantitative effects of iodide on development. It was therefore necessary to devise a method whereby the amounts of iodide transferred to the film via Bimat web material could be accurately determined. Initially, two possible procedures presented themselves. The Bimat web material could be weighed before being placed in the iodide solution and then weighed again after being removed and cleared by a nitrogen squeegee.

The other technique would involve potentiometric titrations of representative Bimat web material both before and after transfer of iodide solution to the test film to determine completion of transfer.

The first technique seemed to be the better at first, because potentiometric titration requires much more time and effort, and it might not be more accurate. Determination of iodide transfer by making weight determinations depended on several factors which required analysis. The time interval between removal of the Bimat from solution and subsequent weighing introduced a weight loss error due to evaporation. This could be easily remedied by producing a graph showing weight loss per unit area of solution-soaked Bimat material as a function of time (Figure 3) and using this to make the appropriate calculation corrections. Also, the density of iodide solutions increases with increasing concentration, and it was anticipated that the volume of solution taken up by the Bimat material would be a function of KI concentration due to the effect of salts on the swelling of emulsions. The graph in Figure 4 (corrected for change in solution density and weight loss due to evaporation) indicates the weight of solution taken in by Bimat web material as a function of KI concentration at 73° Fahrenheit. The data is found in Table 3.

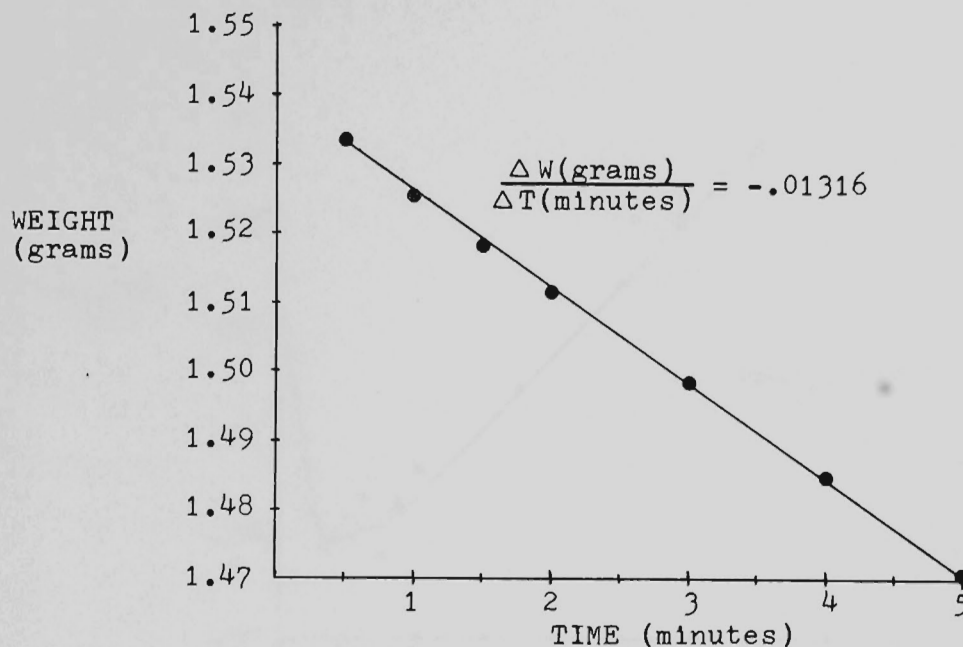


FIGURE 3. An example of evaporation from 4" pieces of 70 mm Bimat web material which were soaked in distilled water for 8 minutes at 73° F.

TABLE 2. Change in weight of 4" pieces of Bimat web material which had been soaked in distilled water for 8 minutes at 73° F. The average is plotted in Figure 3.

TIME	RUN#1	RUN#2	RUN#3	AVERAGE
:30	1.5368	1.5331	1.5304	1.5334
1:00	1.5280	1.5255	1.5223	1.5253
1:30	1.5203	1.5189	1.5155	1.5182
2:00	1.5129	1.5133	1.5087	1.5116
3:00	1.5000	1.5008	1.4946	1.4985
4:00	1.4860	1.4869	1.4814	1.4848
5:00	1.4710	1.4739	1.4661	1.4703

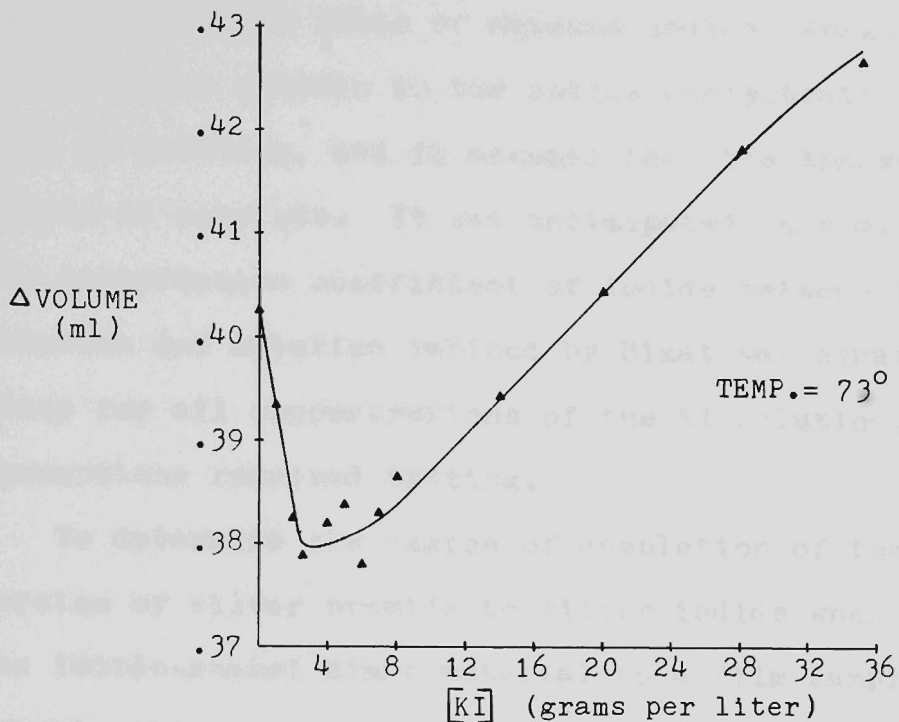


FIGURE 4. Solution intake of Bimat web material for various concentrations of KI. Each point represents the average of three carefully controlled Bimat strips (4 inches of 70mm Bimat material) soaked in iodide solutions for 8 minutes and weighed to determine weight increase. The weights were corrected for evaporation and solution density changes due to changing concentration.

TABLE 3. Data for Figure 4.

[KI] (grams/liter)	ΔVOLUME (average)	[KI] (grams/liter)	ΔVOLUME (average)
0	.4025	7	.3827
1	.3934	8	.3864
2	.3890	14	.3942
3	.3787	20	.4043
4	.3819	28	.4182
5	.3837	35	.4270
6	.3779		

The weight determination procedure depends on the magnitude of the ratio of aqueous iodide concentration in the Bimat gelatin to the iodide concentration of the bulk KI solution, and it assumes that the transfer of iodide is complete. It was anticipated initially that the distribution coefficient of iodide between free solution and solution imbibed by Bimat was equal to unity for all concentrations of the KI solution. These assumptions required testing.

To determine the degree of completion of the conversion of silver bromide to silver iodide when contacting the iodide-soaked Bimat material to a film sample, an experiment was undertaken in which potentiometric titration was used to analyze the Bimat material for residual iodide after transfer. Four inch samples of 70mm Bimat material were soaked in solutions of 5.75 grams and 13.91 grams of potassium iodide per liter for ten minutes. The Bimat material was then squeegeed and contacted to Cine Positive 5302 35mm film for approximately fifteen minutes. After this, the Bimat samples were separated from the Cine Positive film, cut into easily handled strips, and soaked in 25ml of distilled deaerated water. A total of four 25ml soakings were accomplished per sample and the aqueous solution collected after each soak. The solutions were then analyzed for halide content by potentiometric silver nitrate titration with a Beckman Research pH Meter

(Figure 5 and Figure 6). When titrating the halide solution with $1 \times 10^{-2} N$ silver nitrate solution, a silver electrode and a potassium nitrate filled reference electrode were used. Similarly, for each concentration four inch samples of 70mm Bimat material, soaked in the iodide solution and squeegeed, were extracted and analyzed for potassium iodide. Two replications of this procedure were undertaken. The values are found in Table 13.

As indicated in Figure 6 and Table 5, there was very little iodide remaining in the Bimat after transfer for the 13.91 gram/liter KI solution. The equivalence point was reached before .1 milliliters of 1×10^{-2} molar $AgNO_3$ had been used in the titration of the iodide transfer samples. The control strips in Figure 6 contained molar amounts of iodide equivalent to 4.7 milliliters of 1×10^{-2} molar silver nitrate. Thus, less than two percent ($\frac{1}{4.7} \times 100$) of the original iodide remained in the Bimat after transfer.

The potentiometric titration of iodide remaining in Bimat after transfer for a 5.75 grams/liter KI concentration is shown in Figure 5. The end point could not be ascertained due to the extremely small amount of iodide remaining in the Bimat. It was therefore considered adequate to assume that the transfer of iodide between Bimat and Cine Positive was complete.

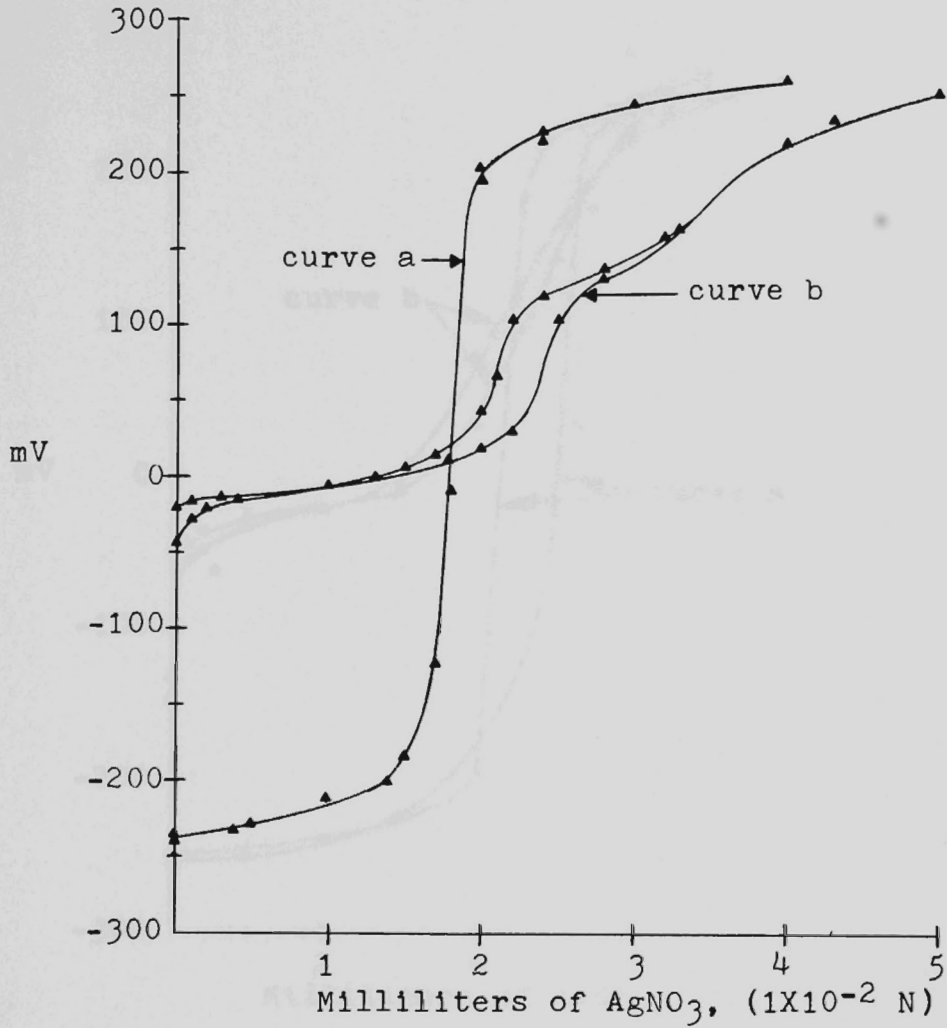


FIGURE 5. Potentiometric titration of extractions of 4 inch samples of 70 mm Bimat material soaked in a 5.75 gram/liter solution of potassium iodide. Two extractions were titrated for Bimat samples before transfer to Cine Positive film, curve a, and two extractions were titrated for Bimat samples allowed to transfer its iodide to Cine Positive, curve b.

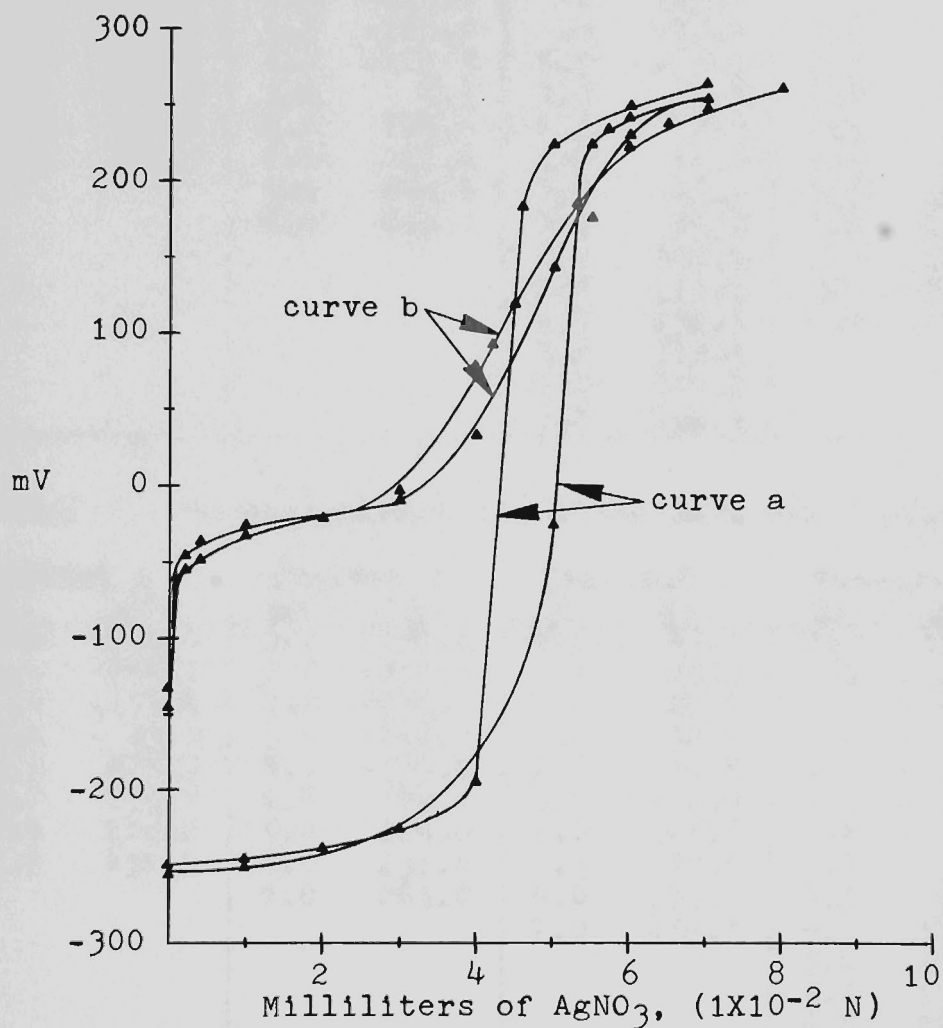


FIGURE 6. Potentiometric titrations of extractions from 4 inch samples of 70 mm Bimat material soaked in a 13.91 grams/liter solution of potassium iodide. Two extractions were titrated for Bimat samples before transfer to Cine Positive film, curve a, and two extractions were titrated for Bimat samples which were allowed to transfer their iodide to Cine Positive, curve b.

TABLE 4. Potentiometric titration data for Figure 5.

Control 1		Control 2		Transfer 1		Transfer 2	
ml	mV	ml	mV	ml	mV	ml	mV
0.0	-235.5	0.0	-240.0	0.0	-43.3	0.0	-20.0
.4	-232.0	.5	-228.7	.1	-27.6	.1	-15.8
1.0	-210.9	1.0	-213.8	.2	-21.0	.3	-12.8
1.4	-200.4	1.5	-183.0	.4	-15.4	1.0	- 4.5
2.0	204.1	1.7	-122.3	1.0	- 5.6	1.5	4.0
2.4	221.3	1.8	8.4	1.3	1.8	1.8	12.2
3.0	246.4	2.0	196.0	1.5	7.3	2.0	19.2
4.0	261.5	2.4	228.2	1.7	15.2	2.2	31.0
		3.0	246.4	2.0	43.4	2.5	104.6
		4.0	262.1	2.1	67.2	2.8	132.0
				2.2	103.0	3.3	164.0
				2.4	119.3	4.0	218.7
				2.8	137.7	4.3	234.6
				3.2	158.4		
				4.0	221.0		
				5.0	252.4		

TABLE 5. Potentiometric titration data for Figure 6.

Control 1		Control 2		Transfer 1		Transfer 2	
ml	mV	ml	mV	ml	mV	ml	mV
0.0	-248.4	0.0	-256.6	0.0	-145.0	0.0	-133.7
1.0	-244.7	1.0	-250.4	.2	-56.3	.1	- 61.4
2.0	-238.0	2.0	-241.3	.4	-48.4	.2	- 46.0
5.0	- 23.0	3.0	-226.3	1.0	-32.9	.4	- 36.5
5.5	225.9	4.0	-193.0	2.0	-20.8	1.0	- 26.8
5.7	233.7	4.6	184.0	3.0	- 8.4	2.0	- 16.8
6.0	242.2	5.0	224.0	5.0	145.0	3.0	- 3.3
7.0	257.2	6.0	251.4	5.3	187.4	4.0	33.5
		7.0	265.0	6.0	232.5	4.2	94.0
				7.0	254.8	4.5	119.5
						5.0	142.5
						5.5	177.7
						6.0	223.7
						6.4	240.5
						7.0	250.5
						8.0	262.0

By referring to Figure 3 and Figure 4, it is possible to estimate the volume of solution taken in by the Bimat strips and consequently the expected amount of iodide being titrated. For 5.75 grams of KI per liter, .3805 milliliters of solution should be absorbed which corresponds to 2.19×10^{-3} grams of KI. However, 3.0×10^{-3} grams of KI were found by potentiometric titration. This is 1.37 times more than was expected. For the 13.91 grams KI per liter concentration, .394 milliliters of solution should be absorbed, which is equivalent to 5.48×10^{-3} grams of iodide. But 7.802×10^{-3} grams of iodide were determined via potentiometric titration. This is 1.42 times the amount which was expected. The reason for these discrepancies must be that the aqueous concentration of iodide in the Bimat material is not the same as in the bulk solution.

Because the distribution coefficient for iodide in a gelatin-aqueous solution environment was greater than 1.0, it was necessary to use potentiometric titrations of Bimat soaked in iodide solutions of varied concentrations to establish the amounts of iodide actually transferred to film. Weight determination of iodide transferred was therefore abandoned. Potentiometric titration of one concentration of iodide would not have been sufficient because it was not certain that the iodide distribution coefficient between Bimat absorbed solution

and free solution was independent of concentration. Knowledge of the distribution coefficients as a function of concentration would be sufficient in itself to enable the determination of mole percent iodide transferred because the conversion is essentially complete as was indicated in Figure 5 and Figure 6. The results of the potentiometric titrations are shown in Table 6, and the data is plotted in Figure 7.

From these experiments and determination of the emulsion coating weights (grams of silver per unit area), it would be possible to calculate the concentrations of potassium iodide Bimat soak solutions necessary to accomplish the conversion of a known mole percent of the emulsion silver bromide to silver iodide.

Silver and Iodide Analysis

To express the transfer of iodide in terms of mole percent of the total halide present in the emulsion, potentiometric titration analysis for silver per unit area was undertaken for both emulsions, Cine Positive 5302 Film and Panatomic X Film (Appendix B). It was determined from two replications that the Pan X coating weight was approximately 2.94 grams of silver per square meter, and the Cine Positive 5302 film had a coating weight of 3.90 grams of silver per square meter. The original mole percent of iodide composition of the two films was

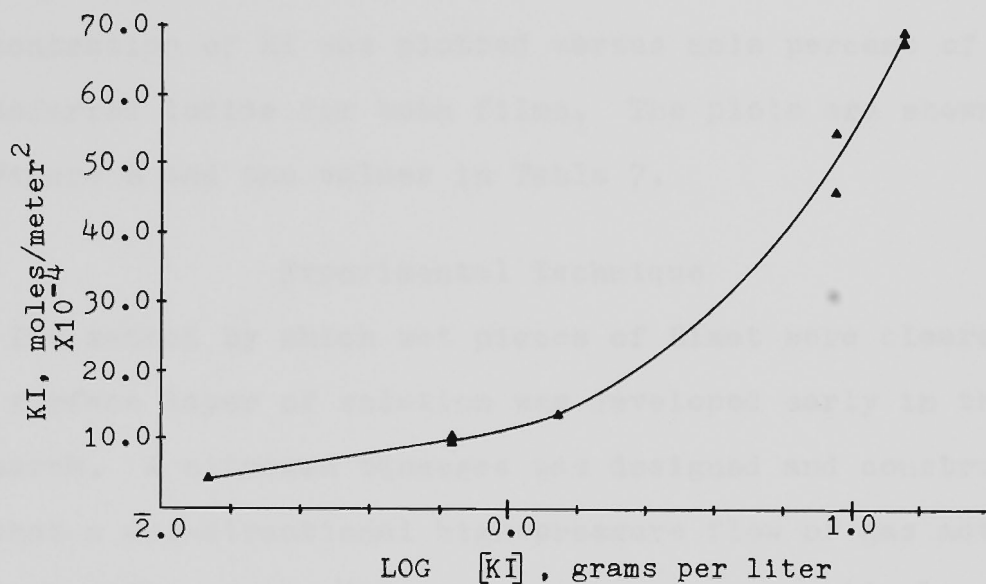


FIGURE 7. This graph shows the number of moles of potassium iodide per square meter extracted from Bimat material versus the logarithm of the concentration (grams per liter) of the potassium iodide solution in which the Bimat had been soaked. The data was obtained via potentiometric titrations with silver nitrate.

TABLE 6. Data for Figure 7.

Log [KI] (grams/liter)	Run #1 moles KI/meter ²	Run #2 moles KI/meter ²	Average moles/meter ²
1.1350	4.06X10 ⁻⁴	3.91X10 ⁻⁴	3.98X10 ⁻⁴
1.8414	9.58X10 ⁻⁴	10.63X10 ⁻⁴	10.10X10 ⁻⁴
.1483	13.66X10 ⁻⁴	13.76X10 ⁻⁴	13.71X10 ⁻⁴
.9542	54.43X10 ⁻⁴	46.12X10 ⁻⁴	50.27X10 ⁻⁴
1.1440	67.75X10 ⁻⁴	69.08X10 ⁻⁴	68.41X10 ⁻⁴

reported ²⁴ as 1.13 and 5.82 mole percent for Cine Positive and Pan X Films, respectively. Using the values for silver coating weight and the data in Table 6, the free solution concentration of KI was plotted versus mole percent of transferred iodide for both films. The plots are shown in Figure 8 and the values in Table 7.

Experimental Technique

The method by which wet pieces of Bimat were cleared of the surface layer of solution was developed early in the research. A nitrogen squeegee was designed and constructed so that a uni-directional high pressure flow of gas acting on both sides of the film stripped away any residual moisture. The squeegee proved to be quite successful, and of course, its importance in enabling a uniform transfer of iodide is quite obvious.

The technique of transferring iodide to the two film types (Pan X and Cine Positive) required practice to attain proficiency. The procedure used throughout this research was simple, but time consuming.

Each run consisted of preparation of eight film test strips which contained various amounts of transferred iodide, or none at all. Bimat strips approximately six inches long and approximately 23mm wide were allowed to soak for at least ten minutes in solutions of $5 \times 10^{-4} N$ potassium bromide solution together with various concentrations of potassium iodide. Each strip of Bimat in turn

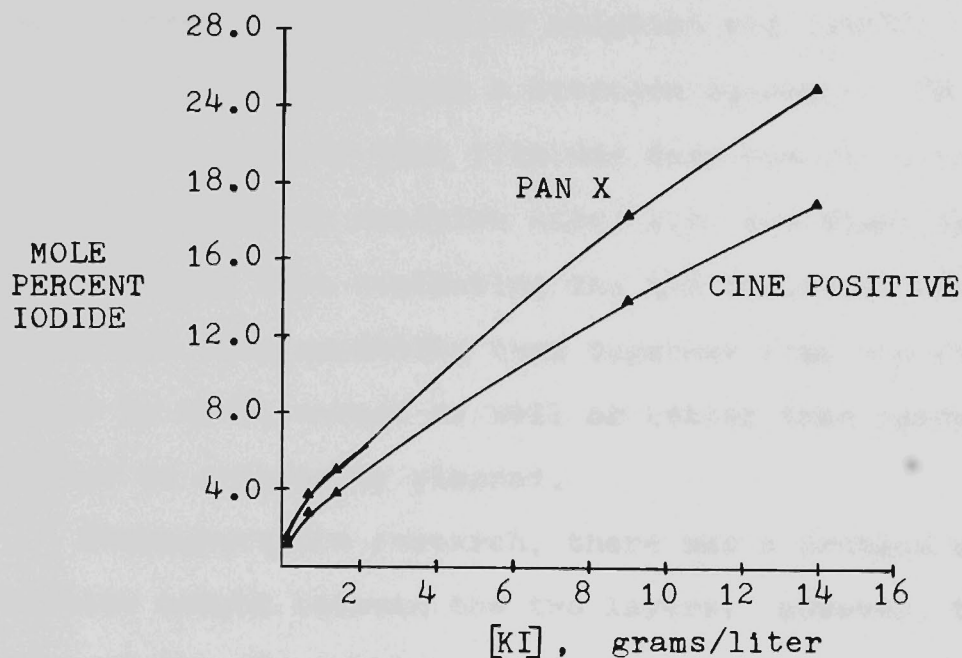


FIGURE 8. The amount of iodide transferred to either Pan X or Cine Positive film from Bimat material for given concentrations of KI used as the soak. Two replications were made at each level and the average plotted here.

TABLE 7. Data for Figure 8.

[KI] gms/liter	1		2		Average	
	CP	PAN X	CP	PAN X	CP	PAN X
.1364	1.12	1.48	1.083	1.43	1.10	1.46
.694	2.65	3.51	2.94	3.89	2.79	3.70
1.407	3.78	5.00	3.81	5.04	3.80	5.02
9.00	15.08	19.93	12.77	16.88	13.93	18.40
13.91	18.77	24.81	19.14	25.30	18.96	25.05

was removed from its halide solution and quickly cleared of surface moisture with a nitrogen squeegee. An exposed five inch piece of 35mm film was then placed in contact (emulsion side to emulsion side) with the Bimat material. It was found that contacting the two strips at one end first and then smoothing them together from one end to the other by hand, worked as well or better than using a print roller as originally planned.

Throughout the research, there was a problem with air bubbles caught between the two layers. However, the location of the air bubbles could be readily determined after development, and densitometer readings could normally be taken in the more homogeneous areas of the film. After contacting the test film strip to the Bimat material, the combination was placed upon a flat piece of heavy plate glass, and an attempt was made to smooth out air bubbles. Having accomplished this, another piece of plate glass was used to sandwich the Bimat and film for at least fifteen, but not more than twenty, minutes (any longer and the emulsion tended to pull off when separation was attempted).

At the end of the desired time of contact, the Bimat and the test film strip were separated, the Bimat material discarded, and the test film strip hung in a light-tight cabinet until needed for development.

Considerable care was required to assure the proper development temperature. The nitrogen burst tank temperature was intentionally biased by running water through it with a temperature which would tend to counteract the differential between the ambient air temperature and the desired temperature of development (72° Fahrenheit in all cases). The developer (800cc) was first brought to 72° Fahrenheit. After using a small amount of the developer to prerinse the nitrogen burst tank, the developer was poured into the tank and its temperature monitored until development was begun. In the meantime, the test strips were removed from their light-tight cabinet and placed emulsion side outward on the nitrogen burst tank film carrier, which had also been temperature biased. A darkroom timer was started at time zero as the film carrier was lowered into the developer tank and the nitrogen burst sequence was begun. A burst interval of eight seconds and a burst duration of 1.2 seconds were set for all experimental runs. At the end of the desired development period, the film carrier was quickly removed from the nitrogen tank and placed in an acid stop bath for approximately 30 seconds. The carrier, still bearing the eight test strips, was transferred to an acid fix (Kodak F-6 Fixer) for approximately four minutes and then washed thoroughly for at least six minutes. Finally, the strips were placed in photoflo solution and hung up to

dry in a drying cabinet.

Iodide Induced Spectral Absorption Changes

Iodide transfer will change the spectral absorption and hence the reflectivity of an unexposed, undeveloped photographic emulsion. To demonstrate this, a set of film samples were prepared which contained a range of transferred amounts of iodide and $5 \times 10^{-4} \text{N}$ KBr. Both Cine Positive 5302 and Panatomic X film were used. A Beckman DK 2A Spectrophotometer was operated in a reflection mode with a white barium sulphate reference to show the spectral reflectivity of the samples in the wavelength region from 350nm to 700nm. In both cases, as indicated in Figure 9 and Figure 10, the effect of increased iodide transfer was an increase in absorption in the violet with a sharp edge at 430nm. The location of the absorption edge corresponds to the data in the literature²⁵ for the optical absorption edge for nominally pure evaporated silver iodide layers. The absorption for a mixed crystal of AgI and AgBr extends to longer wavelengths²⁶ and does not have the sharp edge of pure silver iodide, as shown by the reflectance of the controls; note the stronger absorption of the Pan X for longer wavelengths. Consequently, the 430nm absorption edge is evidence that the transfer of iodide to the emulsion creates pure silver iodide somewhere in the emulsion.

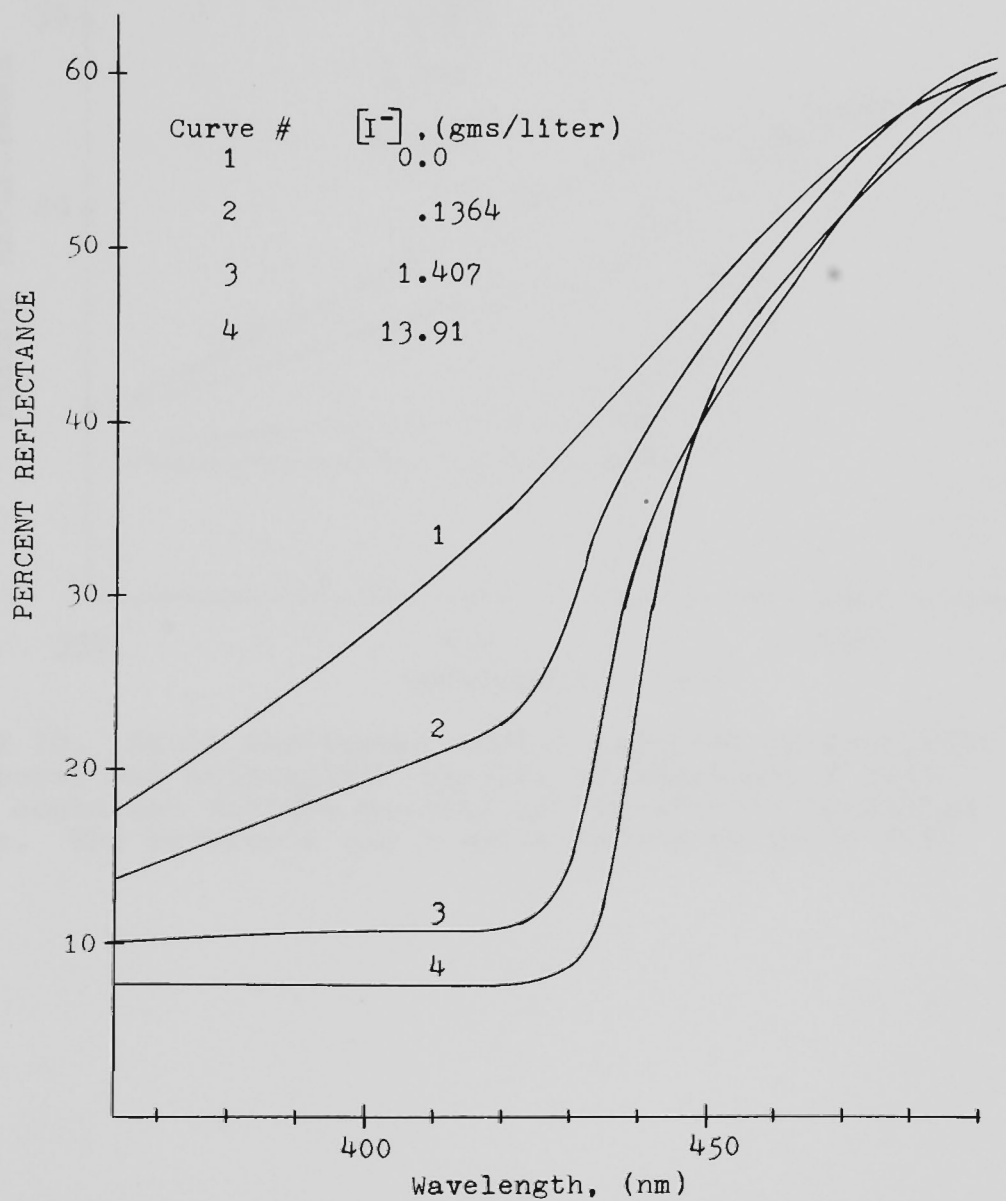


FIGURE 9. DK-2A Spectrophotometer spectral reflectivity of exposed but undeveloped samples of Cine Positive film which contained various amounts of transferred potassium iodide. The reference was a white barium sulphate disc.

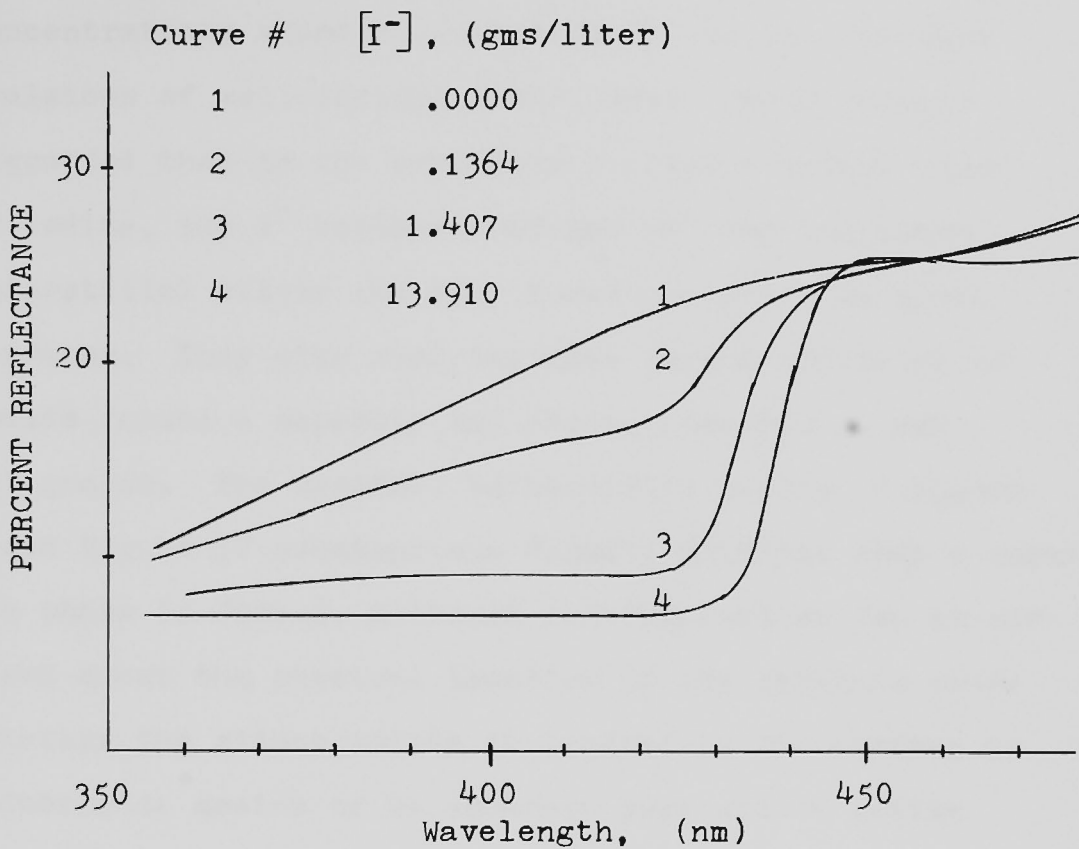


FIGURE 10. DK-2A Spectrophotometer spectral reflectivity of exposed but undeveloped samples of Panatomic X film which contained various amounts of transferred potassium iodide. The reference was a white barium sulphate disc.

Mumaw²⁷ investigated the effect of iodide in varying concentrations added to coated cubic and tabular AgBr emulsions of well-defined grain size. Their results suggested that in the monolayer surface coverage range of iodide, the I^- replaces surface Br^- and increases interstitial silver ion concentrations near the grain surfaces. They also reported that larger additions of iodide formed a separate AgI phase, possibly as new AgI grains. The spectral reflectivity curves in Figure 9 and Figure 10 substantiate Mumaw's evidence that a separate phase is formed, although nothing further can be surmised about the physical location of the separate phase (whether the silver iodide is located on the surface of iodobromide grains or as separate pure silver iodide grains).

Iodide Transfer Series

One of the first experiments conducted after the initial preliminary investigations was designed to determine the effect on development of iodide transfer to Cine Positive film for a wide range of iodide concentrations. Six solutions of potassium iodide were prepared for transfer to the film. In this experiment, 5×10^{-4} N KBr was added to the iodide solutions including controls to maintain an approximately constant concentration of bromide ion in the film. The choice of

$5 \times 10^{-4} \text{N}$ was made more or less arbitrarily, but with the knowledge (based on advice by Dr. B. H. Carroll who has considerable experience in emulsion making) that many iodobromide emulsions contain about this concentration of bromide ion. Two test strips were used as controls. One was merely exposed and then developed. The other strip was exposed first, and then contacted with Bimat film soaked in a 5×10^{-4} normal solution of KBr. The controls help to account for differences which might occur because of a loss of other emulsion constituents during the transfer procedure. The developer chosen for this purpose was DK-50, used full strength for a development time of three minutes at 72° Fahrenheit. The nitrogen burst development was accomplished using a burst duration of 1.2 seconds and a burst interval of eight seconds (these burst times were used throughout the research). The exposures which preceded the transfer of iodide were made using a Kodak Model 101 Process Control Sensitometer (2850° K) and a 21 step Kodak #2 Step Tablet which had been calibrated on a Macbeth TD 102 Densitometer. The results are shown in Figure 11.

In the preliminary experiments with Cine Positive, several problems became apparent. One of these was the relatively small differences between curves. The experimental variability was high enough that in many cases the significance of the differences between curves

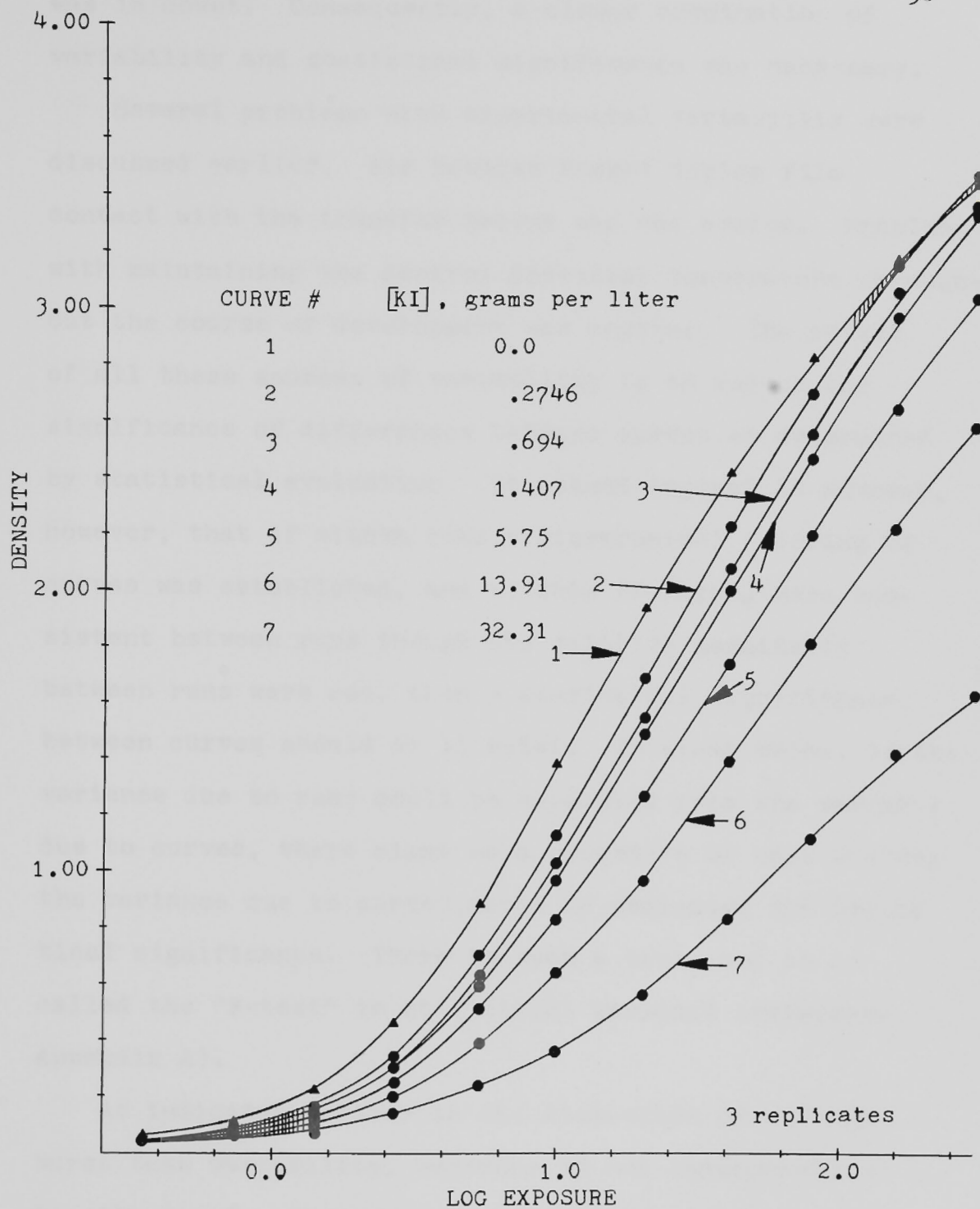


FIGURE 11. Characteristic curves of a potassium iodide transfer series for Cine Positive 5302 film developed in DK 50 developer for three minutes at 72° Fahrenheit (nitrogen burst agitation).

was in doubt. Consequently, a closer examination of variability and statistical significance was necessary.

Several problems with experimental variability were discussed earlier. Air bubbles formed during film contact with the transfer medium was one source. Problems with maintaining the desired developer temperature throughout the course of development was another. The effect of all these sources of variability is to reduce the significance of differences between curves as determined by statistical evaluation. It seemed logical to suppose, however, that if within runs a hierarchical ordering of curves was established, and if this hierarchy were consistent between runs though the relative magnitudes between runs were not, then a statistical significance between curves should still exist. In other words, if the variance due to runs could be separated from the variance due to curves, there might be a procedure or test whereby the variance due to curves could be evaluated for statistical significance. There is such a test, and it is called the "F-test" in statistical parlance (reference Appendix A).

As indicated earlier in the discussion of nitrogen burst tank variability, variance is not independent of density level. It was therefore recognized that a statistical test of differences must be confined to an exposure level locale to be of practical use. Consequently,

an adaptation of the statistical technique known as Analysis of Variance²⁸ was developed to meet the requirements of the situation.

The statistical technique which was developed for use could best be described as a "sliding ANOVA." A standard application of ANOVA was accomplished for each pair of adjacent curves at each pair of adjacent exposure levels in an overlapping manner throughout the exposure range. As a result, each ANOVA solution was a $2 \times 2 \times N$ REPS factorial where N REPS indicated the number of replicates. An F-test for the mean square due to curves was performed against the mean square due to error at an alpha risk of .05. The alpha risk represents the chance one takes of being wrong when the null hypothesis is rejected (here the null hypothesis says there is no difference due to curves). An alpha risk of .05, therefore, means that if the curves are determined to be different by the F-test, then there is a five percent chance that there actually was no difference between curves.

Obviously the sliding ANOVA technique requires a large number of calculations to evaluate multi-curve sets of data. Consequently, a computer program was written to accomplish the necessary calculations (Appendix A). The only outputs necessary were the F-test ratios (Table 8), and these were printed out along with the average of the density readings for the different curves.

The F test ratios plotted against exposure level (Figure 12) provided a ready means of determining the location of insignificant differences between curves, and the results often showed significant differences where the standard deviations of density readings were quite large. This is what makes "sliding ANOVA" a particularly valuable technique for these sets of data. A line was drawn across the graph (Figure 12) to indicate the level below which an F-test ratio must fall before there is an indication that no difference due to curves exists. For the details of ANOVA calculations the reader is referred to Statistics, An Introduction by Rickmers and Todd²⁹, and Appendix A.

The graph in Figure 17 shows the F-test values plotted at the midpoints of adjacent exposures. It is assumed that interpolation is valid for regions where the F-test versus exposure level curves are continuous. Certain areas between curves in Figure 11 were shaded to indicate that there was a lack of statistical significance. In regions of very small differences between curves (such as in the toe of the characteristic curve), it was not found to be practicable to do this, however.

At the highest concentration of transferred iodide, it appeared probable that a further loss of density would result for greater concentrations of iodide. At the lowest concentration it did not appear to be certain that

the curves were approaching the control curve, so that the possibility existed that some acceleration of development would occur at even lower concentrations of iodide. A second iodide transfer series was therefore accomplished for lower concentrations of iodide at three and ten minutes development times. The characteristic curves are shown in Figure 13 and Figure 15. The F-tests for Figure 13 and Figure 15 are shown in Figure 14 and Figure 16, respectively. The values for these graphs are found in Table 9 and Table 10. No consistent acceleration was found at any concentration of iodide, but in the range of densities above a value of 2.5 there is evidence of a slight amount of acceleration for the three lowest concentrations of iodide. The data in Table 9 indicates the magnitude of the apparent acceleration, and the F-tests in Figure 14 confirm that the acceleration is real, at least for the lowest concentration of iodide. An explanation for this acceleration with a Metol-hydroquinone developer is not known. The effect was very small and could even be explained in terms of a change in covering power due to the presence of small amounts of iodide. At ten minutes development time, development retardation by iodide is even more apparent than for the three minute data. Three concentration levels of iodide were chosen from Figure 13 for subsequent experimentation, as it was not deemed practical or especially useful to work with five or six

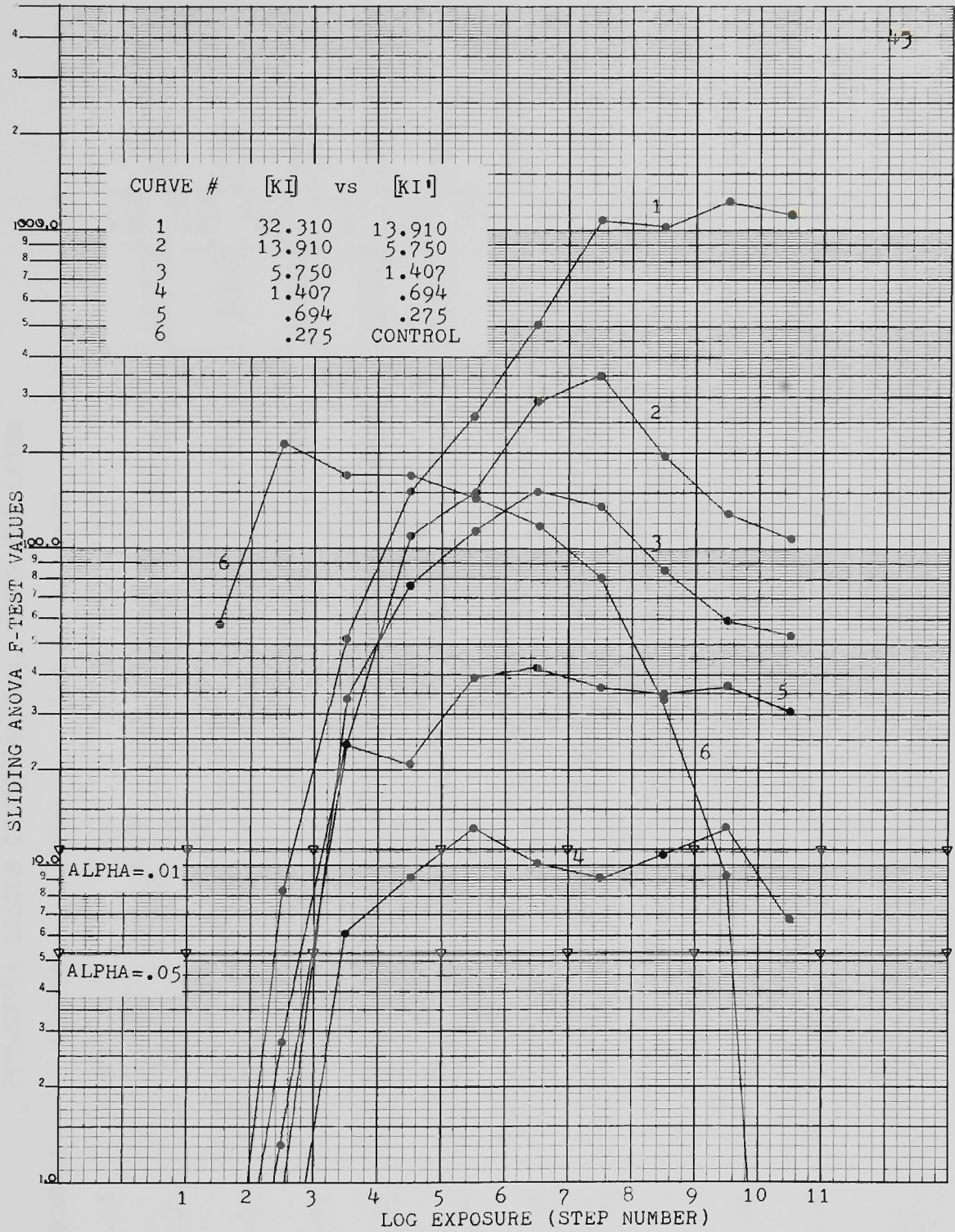


FIGURE 12. Sliding ANOVA F-test values for Figure 11 versus the number of the log exposure step (from Table 8).

POTASSIUM IODIDE CONCENTRATION, GRAMS PER LITER

LOG EXPOSURE	CONTROL	.2746	.694	1.407	5.75	13.91	32.31
1) 1.55	DENSITY s	.06 .000	.04 .000	.05 .000	.05 .000	.05 .000	.05 .000
2) 1.87	F-TEST DENSITY s	.11 .000	.08 .000	.07 .000	.07 .000	.06 .000	.06 .000
3) .15	F-TEST DENSITY s	.22 .006	.16 .011	.13 .006	.12 .006	.10 .015	.07 .006
4) .43	F-TEST DENSITY s	.46 .023	.34 .021	.29 .015	.25 .010	.20 .010	.14 .011
5) .73	F-TEST DENSITY s	.88 .027	.70 .032	.59 .026	.51 .011	.39 .021	.24 .015
6) 1.00	F-TEST DENSITY s	1.38 .049	1.13 .032	.97 .036	.83 .015	.64 .032	.36 .020
7) 1.31	F-TEST DENSITY s	1.94 .049	1.69 .042	1.49 .045	1.27 .029	.97 .027	.56 .026
8) 1.61	F-TEST DENSITY s	2.42 .059	2.23 .031	2.00 .062	1.74 .045	1.39 .032	.83 .015
9) 1.90	F-TEST DENSITY s	2.83 .059	2.70 .036	2.47 .056	2.20 .070	1.81 .040	1.12 .040
10) 2.20	F-TEST DENSITY s	3.18 .051	3.16 .015	2.97 .066	2.65 .094	2.22 .038	1.42 .026
11) 2.48	F-TEST DENSITY s	3.44 .028	3.47 .011	3.33 .061	3.04 .100	2.58 .063	1.63 .045

TABLE 8. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 11.

concentrations. The second, fourth, and sixth concentration levels in Figure 13 were, therefore, chosen as being representative.

In later work the decision to limit the number of levels being tested allowed two test strips to be developed simultaneously for each set of three iodide concentration levels per run. The nitrogen burst tank capacity is eight test strips so two test strips could be run as controls and two test strips could be used for each of the iodide levels being evaluated. The duplicate sets of test strips within each run were treated as duplicates and not as replicates for statistical purposes. True replicates would have to come from different experimental runs.

In general, Figure 11, Figure 13, and Figure 15 indicate that increasing iodide concentration results in development retardation with DK-50 developer at both development times. This would indicate that iodide released during development would, like that transferred before development, retard development of Cine Positive film by DK-50 developer.

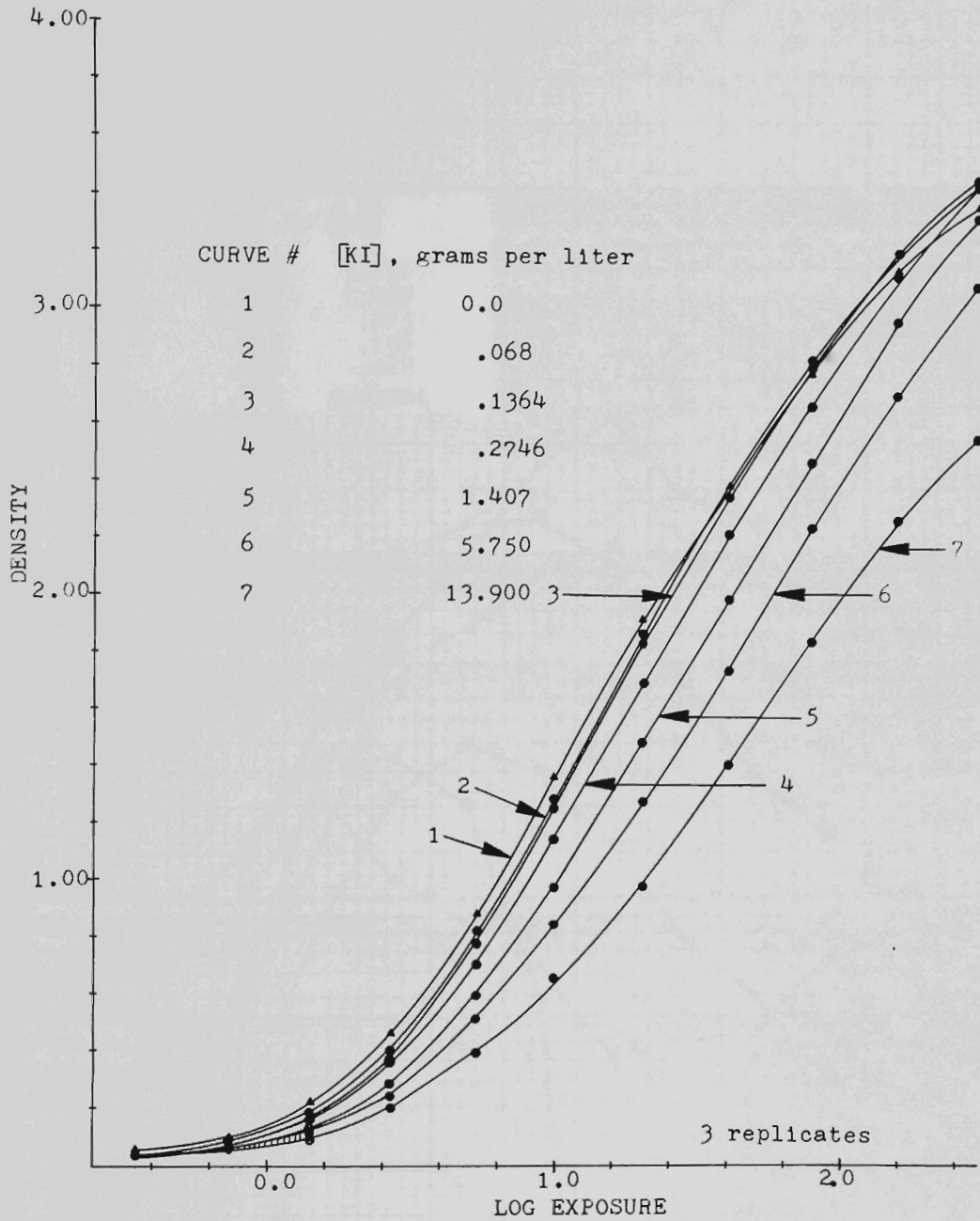


FIGURE 13. Characteristic curves of a potassium iodide transfer series for Cine Positive 5302 film developed in a DK-50 developer for three minutes at 72° Fahrenheit (nitrogen burst agitation).

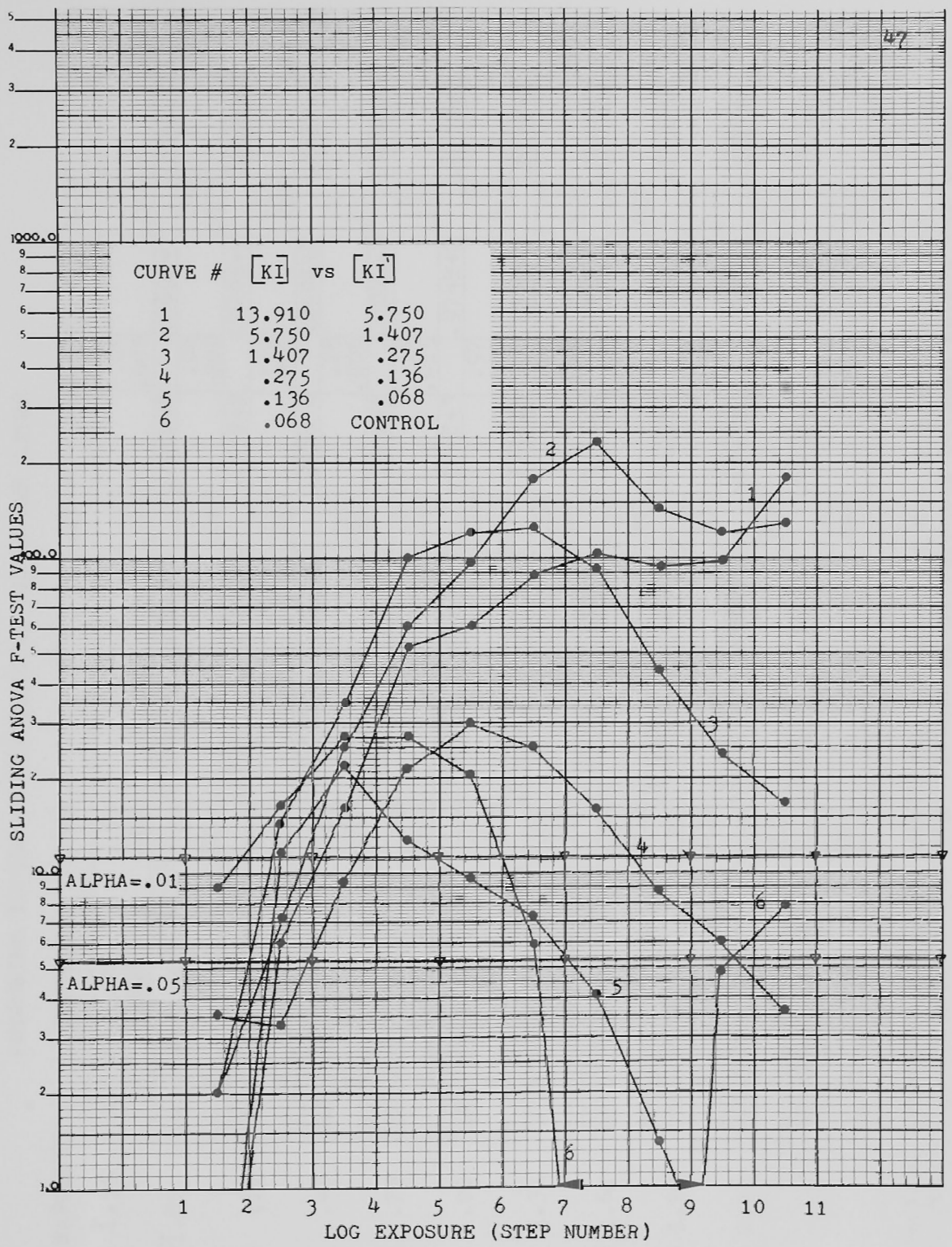


FIGURE 14. Sliding ANOVA F-TEST values for Figure 13 versus the number of the log exposure step (Table 9).

POTASSIUM IODIDE CONCENTRATION, GRAMS PER LITER

LOG EXPOSURE	CONTROL	.068	.1364	.2746	1.407	5.75	13.91
1) 1.55	DENSITY s	.06 .006	.04 .010	.04 .000	.04 .000	.04 .000	.04 .000
2) 1.87	F-TESTS s	.900E+1 .10 .010	.444E 0 .08 .011	.100E+1 .07 .010	.200E+1 .06 .000	.500E 0 .06 .005	.04 .05 .006
3) .15	F-TEST s	.163E+2 .22 .015	.116E+2 .18 .006	.328E+1 .15 .010	.143E+2 .13 .006	.600E+1 .11 .010	.09 .09 .006
4) .43	F-TEST s	.270E+2 .46 .027	.217E+2 .40 .000	.937E+1 .36 .026	.347E+2 .28 .006	.162E+2 .24 .011	.20 .20 .020
5) .73	F-TEST s	.271E+2 .88 .038	.125E+2 .82 .027	.213E+2 .70 .015	.100E+3 .59 .015	.608E+2 .51 .015	.524E+2 .39 .027
6) 1.00	F-TEST s	.204E+2 1.36 .044	.959E+1 1.28 .015	.297E+2 1.14 .029	.120E+3 .97 .027	.613E+2 .84 .015	.65 .65 .061
7) 1.31	F-TEST s	.591E+1 1.91 .072	.726E+1 1.83 .059	.250E+2 1.69 .044	.125E+3 1.48 .006	.883E+2 1.27 .032	.97 .97 .056
8) 1.61	F-TEST s	.560E 0 2.38 .076	.412E+1 2.34 .061	.158E+2 2.21 .061	.923E+2 1.98 .031	.104E+3 1.73 .027	.140 1.40 .080
9) 1.90	F-TEST s	.775E 0 2.77 .061	.137E+1 2.79 .082	.871E+1 2.66 .085	.443E+2 2.46 .038	.943E+2 2.23 .042	1.83 1.83 .091
10) 2.20	F-TEST s	.477E+1 3.13 .036	.602E-1 3.20 .069	.600E+1 3.11 .080	.237E+2 2.95 .045	.948E+2 2.69 .026	2.26 2.26 .102
11) 2.48	F-TEST s	.780E+1 3.35 .056	.866E 0 3.44 .049	.362E+1 3.42 .045	.165E+2 3.31 .050	.181E+3 3.07 .021	2.54 2.54 .062

TABLE 9. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 13.

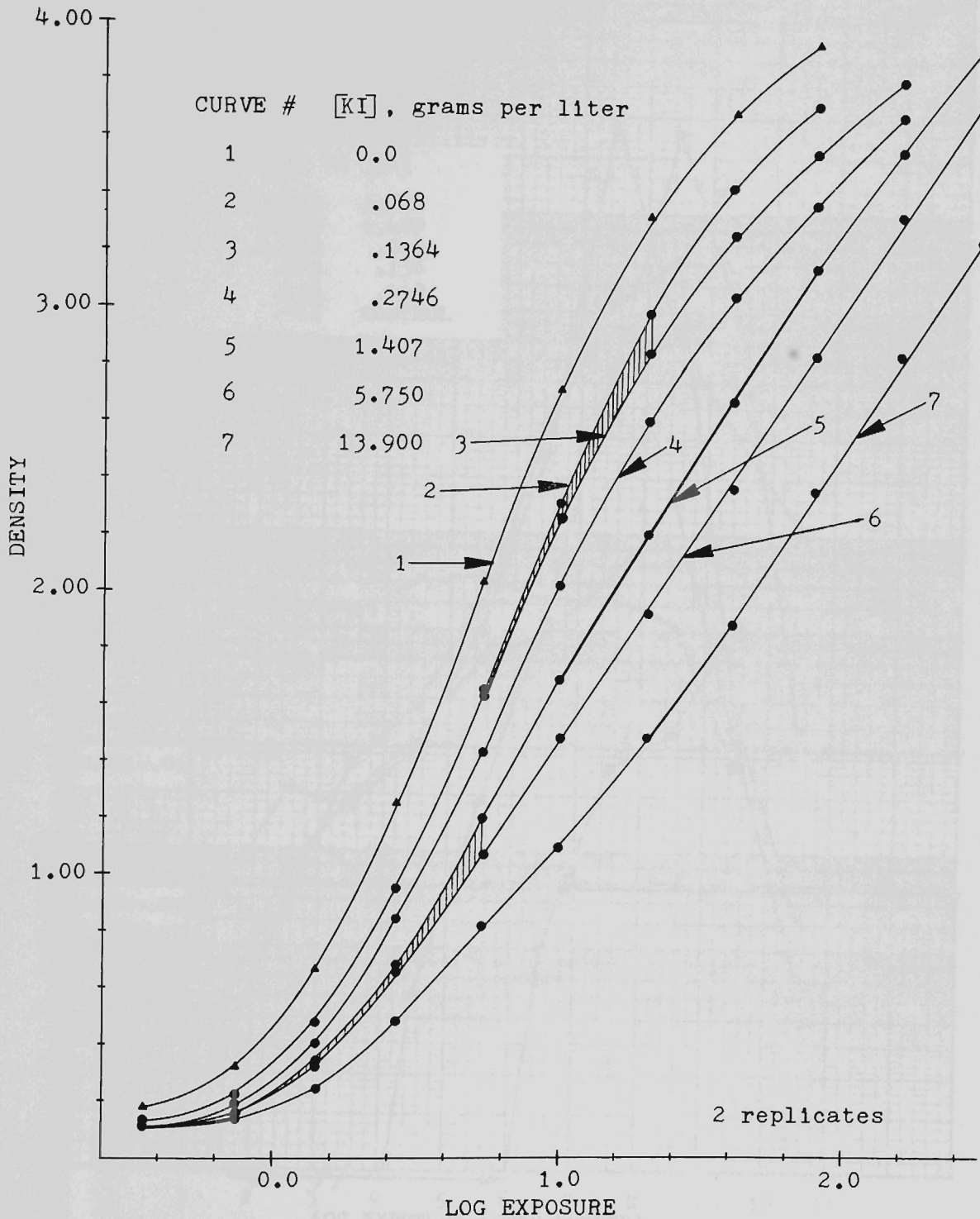


FIGURE 15. Characteristic curves of a potassium iodide transfer series for Cine Positive 5302 film developed in DK-50 developer for ten minutes at 72° Fahrenheit (nitrogen burst agitation).

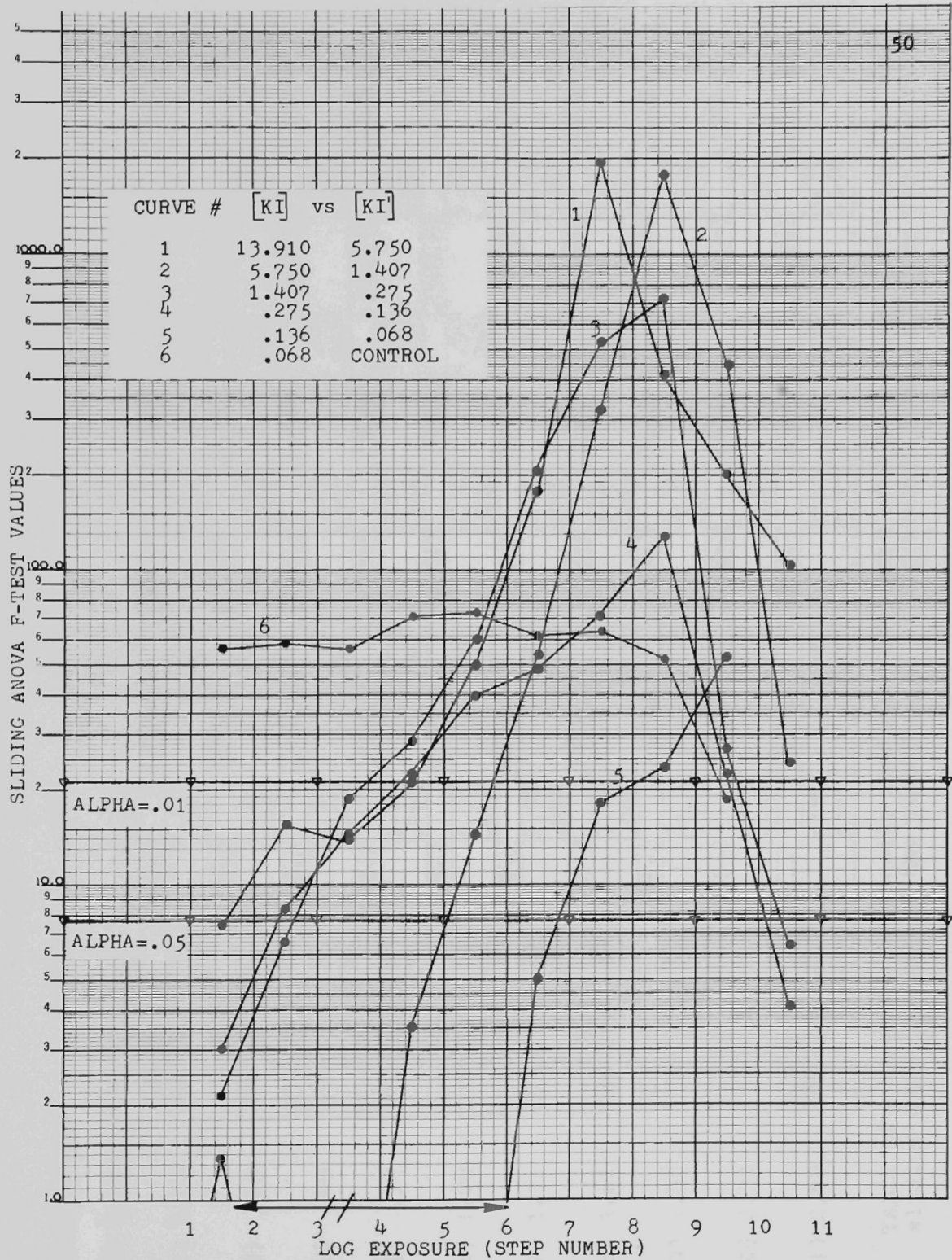


FIGURE 16. Sliding ANOVA F-test values for Figure 15 versus the number of the log exposure step (Table 10).

POTASSIUM IODIDE CONCENTRATION, GRAMS PER LITER

LOG EXPOSURE	CONTROL	.068	.1364	.2746	1.407	5.75	13.91
1) 1.55	DENSITY s	.18 .000	.12 .007	.11 .007	.11 .021	.11 .007	.10 .007
	F-TEST	.560E+2	.133E+1	.300E+1	.213E+1	.392E 0	.736E+1
2) 1.87	DENSITY s	.32 .014	.21 .014	.19 .021	.16 .021	.17 .021	.14 .000
	F-TEST	.580E+2	.163E 0	.826E+1	.648E+1	.171E-1	.152E+1
3) .15	DENSITY s	.66 .021	.46 .021	.40 .028	.34 .028	.32 .035	.24 .014
	F-TEST	.560E+2	-----	.141E+2	.186E+2	.457E 0	.135E+2
4) .43	DENSITY s	1.25 .049	.96 .042	.84 .042	.68 .042	.65 .071	.48 .049
	F-TEST	.711E+2	.352E-1	.241E+2	.282E+2	.344E+1	.206E+2
5) .73	DENSITY s	2.03 .049	1.63 .049	1.43 .049	1.20 .071	1.06 .064	.82 .064
	F-TEST	.733E+2	.723E 0	.391E+2	.600E+2	.142E+2	.493E+2
6) 1.00	DENSITY s	2.71 .078	2.26 .071	2.02 .000	1.69 .057	1.48 .064	1.11 .057
	F-TEST	.616E+2	.492E+1	.482E+2	.201E+3	.527E+2	.175E+3
7) 1.31	DENSITY s	3.32 .071	2.84 .064	2.60 .028	2.20 .035	1.92 .021	1.48 .000
	F-TEST	.638E+2	.177E+2	.705E+2	.526E+3	.318E+3	.192E+4
8) 1.61	DENSITY s	3.68 .035	3.26 .035	3.04 .014	2.67 .000	2.36 .021	1.88 .000
	F-TEST	.519E+2	.232E+2	.126E+3	.713E+3	.174E+4	.410E+3
9) 1.90	DENSITY s	3.92 .007	3.54 .021	3.36 .028	3.14 .000	2.83 .007	2.35 .064
	F-TEST	.185E+2	.518E+2	.221E+2	.263E+2	.439E+3	.199E+3
10) 2.20	DENSITY s	-----	3.79 .000	3.67 .085	3.55 .028	3.32 .021	2.83 .071
	F-TEST	-----	-----	.400E+1	.632E+1	.240E+2	.102E+3
11) 2.48	DENSITY s	-----	-----	-----	3.92 .064	3.70 .106	3.23 .042

TABLE 10. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 15.

III. IODIDE TRANSFER SERIES INVESTIGATION

The next iodide transfer series of interest was undertaken using the same set of exposure and development conditions except that both DK-50 and H₂Q developers were used, and only the three representative iodide concentration levels were tested. Development times of three and ten minutes were used to generate the sets of characteristic curves and corresponding sliding ANOVA plots in Figure 17 through Figure 24, and the tables of values in Table 11 through Table 14. The H₂Q developer pH was adjusted to approximately 10.61 by adding the appropriate amount of an aqueous solution containing sodium hydroxide. Without the addition of sodium hydroxide to raise pH, the activity of the developer was too low to be of any practical use for development times of three and ten minutes.

For a development time of three minutes with H₂Q developer (Figure 21), acceleration of development was observed for the two lowest amounts of transferred iodide. The image tone of the control strip was noticeably different than that of the test strips

containing amounts of transferred iodide. The control strips were brownish in tone, whereas the iodide transfer test strips were more neutral or black. This tone change from brown to black could quite possibly be indicative of a decrease in the relative amount of solution-physical development taking place. A brown tone can indicate more solution-physical development taking place, and solution-physical development is known to result in a lower value of covering power than direct development. Another possible explanation would be that the iodide causes incomplete development of the grains and finer particles. In either case, a change in the structure of the developed image would be occurring, and consequently, the covering power could change. If the two iodide transfer curves which gave acceleration of development have a higher proportion of filamentary silver as a result of a decrease in the amount of solution-physical development, then the noted acceleration might be partially or completely the result of an increase in covering power and not true acceleration. It would therefore be desirable to express the sensitometric results in terms of silver per unit area of the film versus the logarithm of exposure rather than density versus the logarithm of exposure.

One of the most convenient means of evaluating the

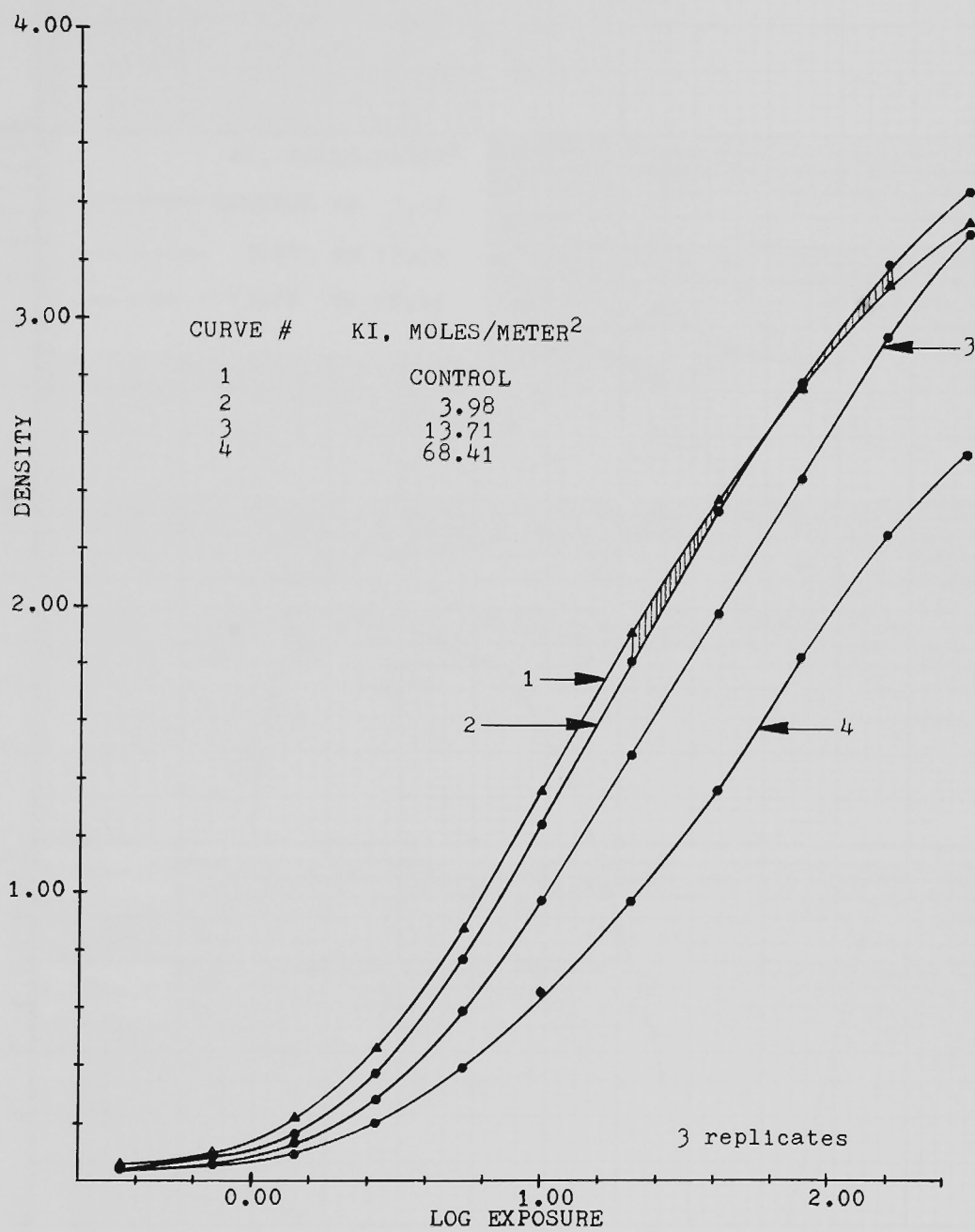


FIGURE 17. Potassium iodide transfer series for Cine Positive film developed in DK-50 for three minutes at 72° Fahrenheit (nitrogen burst agitation).

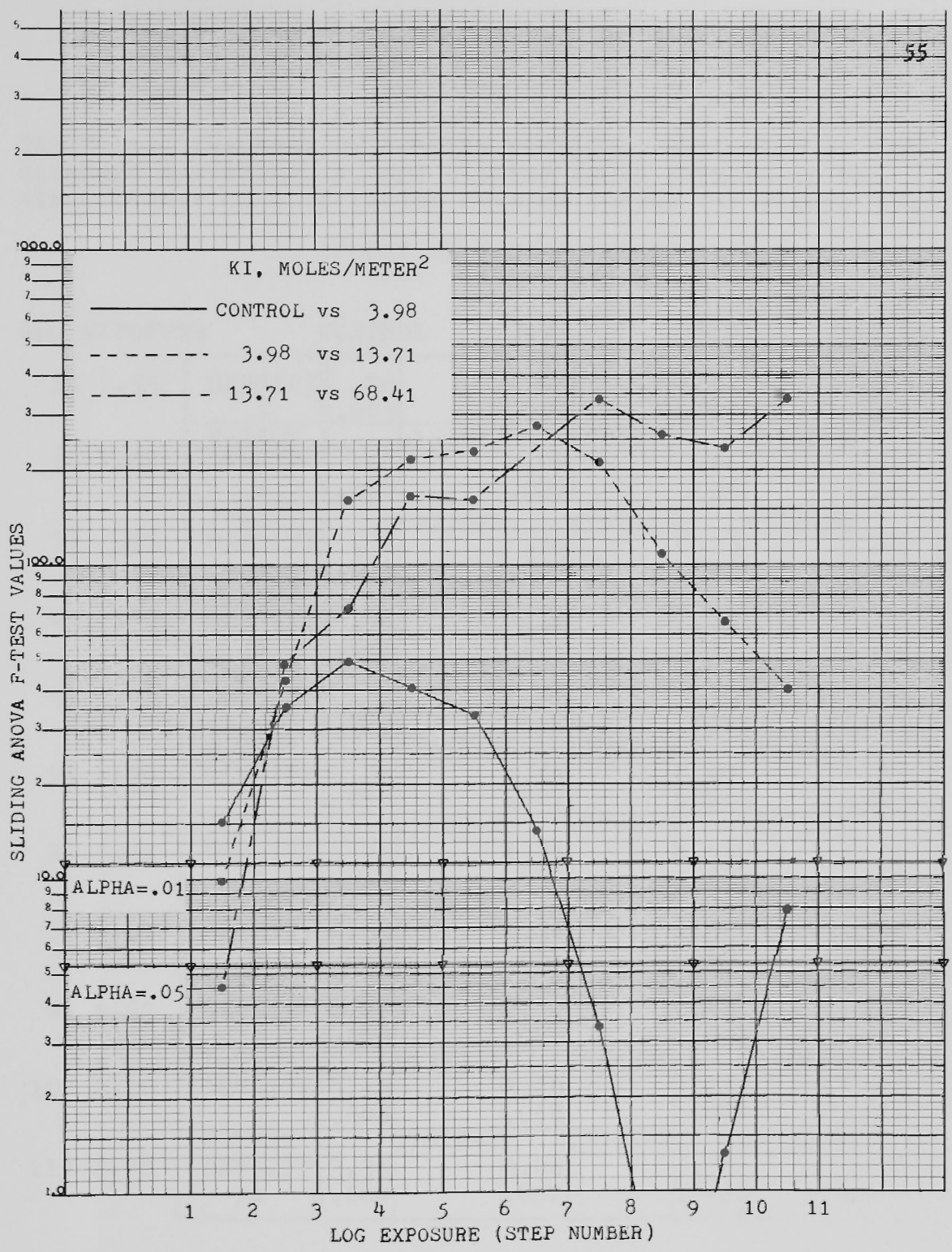


FIGURE 18. Sliding ANOVA F-test values for Figure 17 versus the number of the log exposure step (from Table 11).

TABLE 11. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-TESTS of the significance of differences between curves for Figure 17.

AMOUNT OF IODIDE TRANSFERRED X 10^{-4}
(moles per meter²)

LOG EXPOSURE		CONTROL	3.98	13.71	68.41
1) $\bar{1}.55$	DENSITY	.06	.05	.04	.04
	s	.005	.000	.008	.000
	F-TEST	.151E+2	.980E+1	.450E+1	
2) $\bar{1}.87$	DENSITY	.10	.08	.06	.05
	s	.008	.007	.006	.006
	F-TEST	.353E+2	.427E+2	.480E+2	
3) .15	DENSITY	.22	.16	.13	.09
	s	.011	.006	.006	.012
	F-TEST	.490E+2	.160E+3	.726E+2	
4) .43	DENSITY	.46	.37	.28	.20
	s	.022	.012	.011	.014
	F-TEST	.404E+2	.214E+3	.164E+3	
5) .73	DENSITY	.88	.77	.59	.39
	s	.029	.012	.017	.021
	F-TEST	.331E+2	.228E+3	.160E+3	
6) 1.00	DENSITY	1.36	1.24	.97	.65
	s	.044	.027	.026	.043
	F-TEST	.140E+2	.274E+3	.277E+3	
7) 1.31	DENSITY	1.91	1.81	1.48	.97
	s	.058	.032	.028	.040
	F-TEST	.364E+1	.211E+3	.334E+3	
8) 1.61	DENSITY	2.38	2.34	1.98	1.40
	s	.065	.061	.043	.055
	F-TEST	.827E-1	.108E+3	.259E+3	
9) 1.90	DENSITY	2.77	2.79	2.46	1.83
	s	.064	.086	.040	.064
	F-TEST	.131E+1	.655E+2	.235E+3	
10) 2.20	DENSITY	3.13	3.20	2.95	2.26
	s	.048	.068	.047	.074
	F-TEST	.781E+1	.398E+2	.336E+3	
11) 2.48	DENSITY	3.35	3.46	3.31	2.54
	s	.064	.057	.047	.060

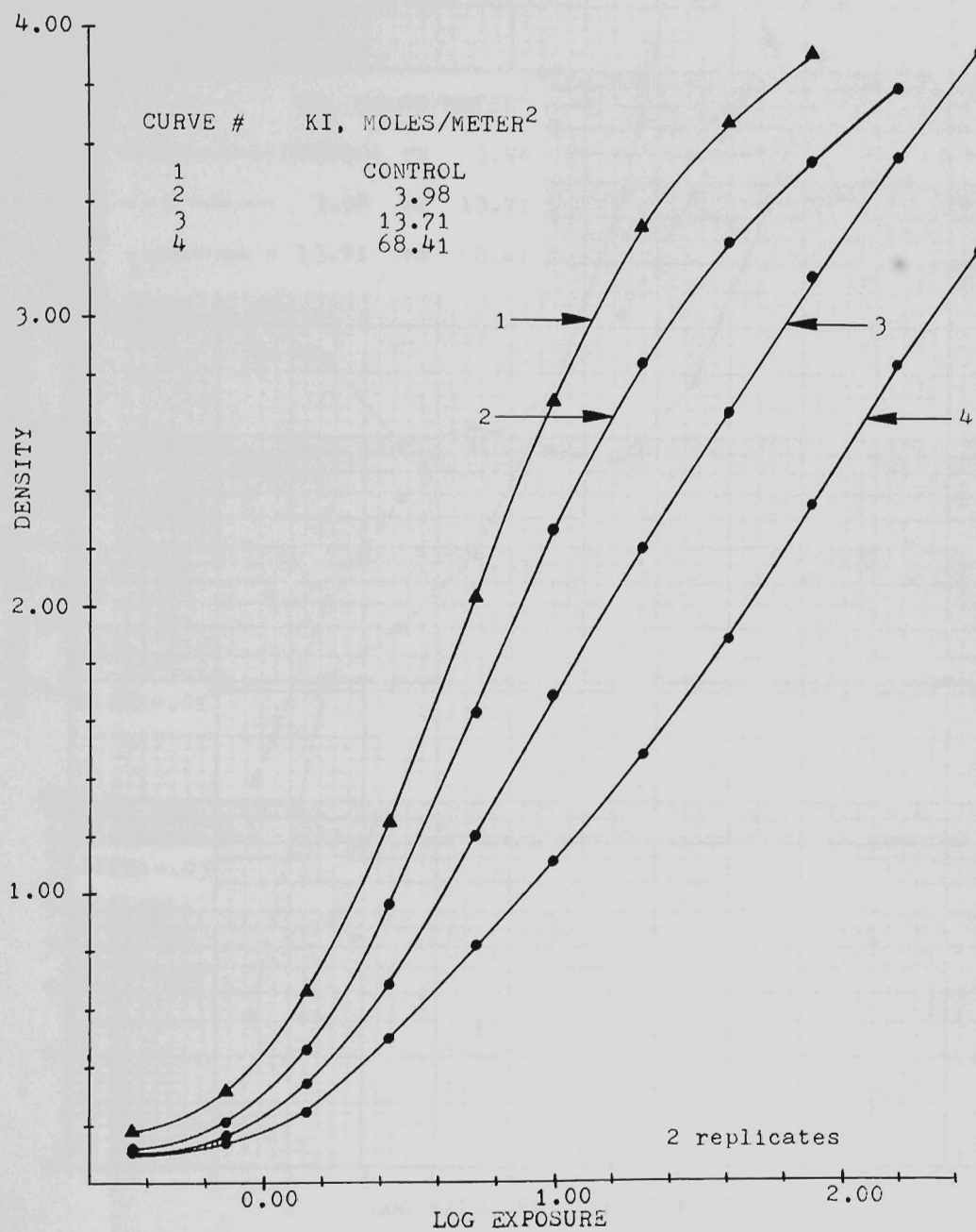


FIGURE 19. Potassium iodide transfer series for Cine Positive film developed in DK-50 for ten minutes at 72° Fahrenheit (nitrogen burst agitation).

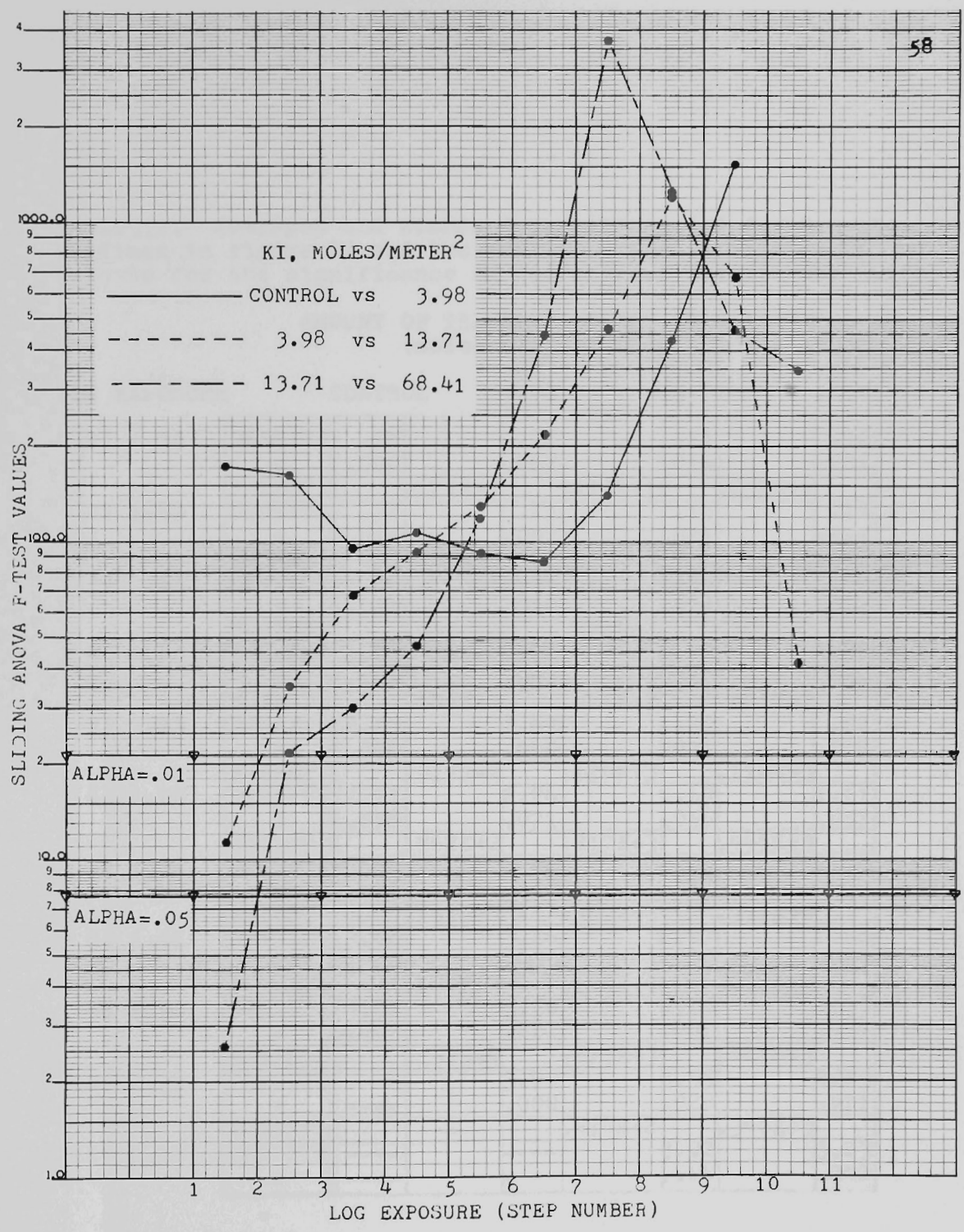


FIGURE 20. Sliding ANOVA F-test values for Figure 19 versus the number of the log exposure step (from Table 12).

TABLE 12. Averages and standard deviations (s) for density readings in Figure 19 and the corresponding sliding ANOVA F-tests for the significance of differences between the curves.

		AMOUNT OF TRANSFERRED IODIDE X 10 ⁻⁴ (moles per meter ²)							
LOG EXPOSURE		CONTROL	3.98	13.71	68.41				
1) 1.55	DENSITY	.18		.12		.11		.10	
	s	.000		.007		.014		.007	
	F-TEST		.171E+3		.113E+1		.257E+1		
2) 1.87	DENSITY	.32		.21		.16		.14	
	s	.014		.007		.021		----	
	F-TEST		.162E+3		.350E+2		.216E+2		
3) .15	DENSITY	.66		.46		.34		.24	
	s	.021		.014		.028		.014	
	F-TEST		.952E+2		.676E+2		.300E+2		
4) .43	DENSITY	1.25		.96		.68		.48	
	s	.049		.042		.042		.056	
	F-TEST		.106E+3		.925E+2		.471E+2		
5) .73	DENSITY	2.03		1.63		1.20		.82	
	s	.049		.049		.071		.064	
	F-TEST		.917E+2		.129E+3		.118E+3		
6) 1.00	DENSITY	2.71		2.26		1.69		1.11	
	s	.078		.071		.056		.057	
	F-TEST		.862E+2		.217E+3		.446E+3		
7) 1.31	DENSITY	3.32		2.84		2.20		1.48	
	s	.071		.064		.035		.000	
	F-TEST		.139E+3		.467E+3		.371E+4		
8) 1.61	DENSITY	3.68		3.26		2.67		1.88	
	s	.035		.035		.000		.000	
	F-TEST		.430E+3		.120E+4		.126E+4		
9) 1.90	DENSITY	3.92		3.54		3.14		2.35	
	s	.007		.021		.000		.064	
	F-TEST		.152E+4		.673E+3		.461E+3		
10) 2.20	DENSITY	----		3.79		3.55		2.83	
	s	----		.000		.028		.071	
	F-TEST		-----		.414E+2		.344E+3		
11) 2.48	DENSITY	----		----		3.92		3.23	
	s	----		----		.064		.042	

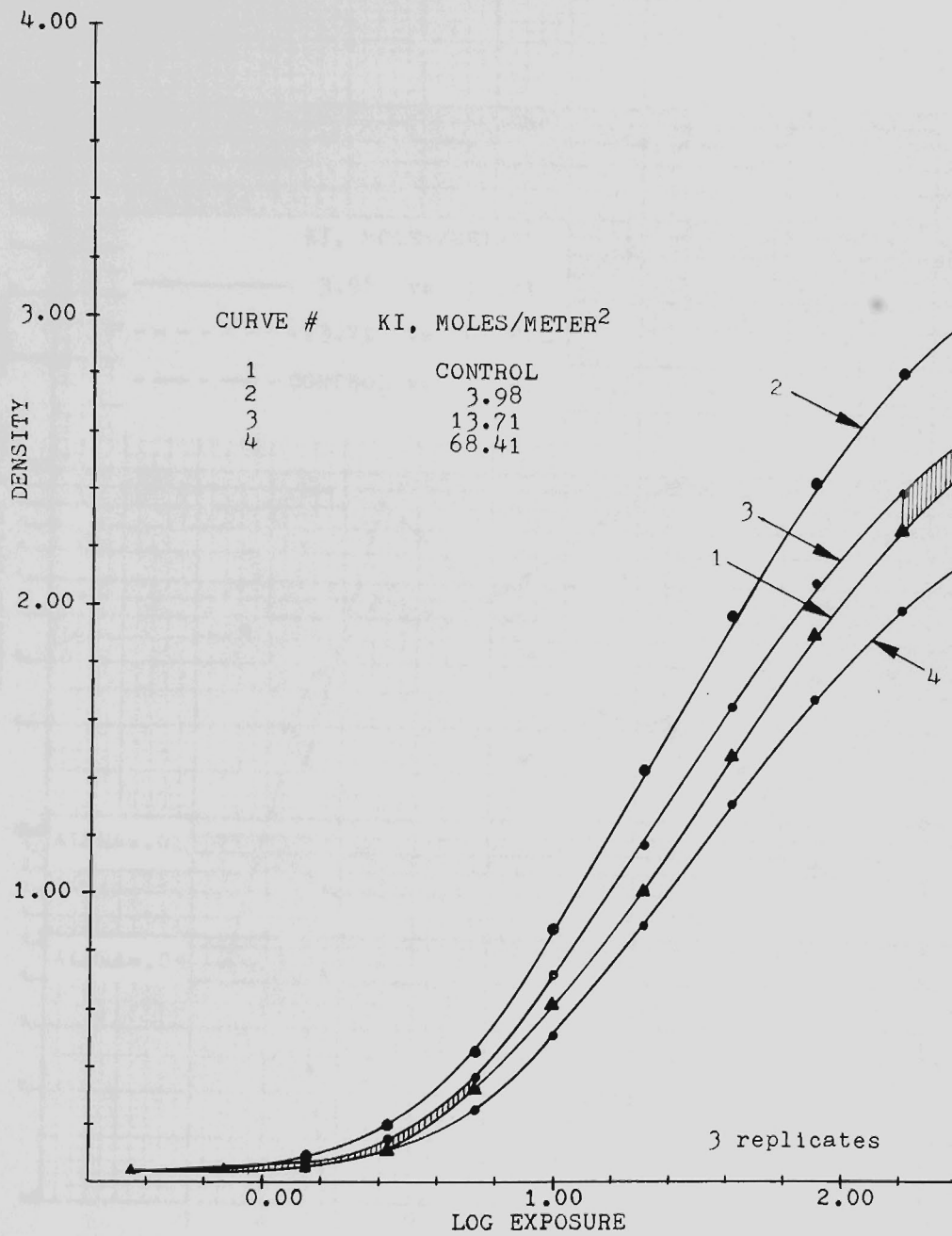


FIGURE 21. Potassium iodide transfer series for Cine Positive film developed in H₂Q developer for three minutes at 72° Fahrenheit (nitrogen burst agitation).

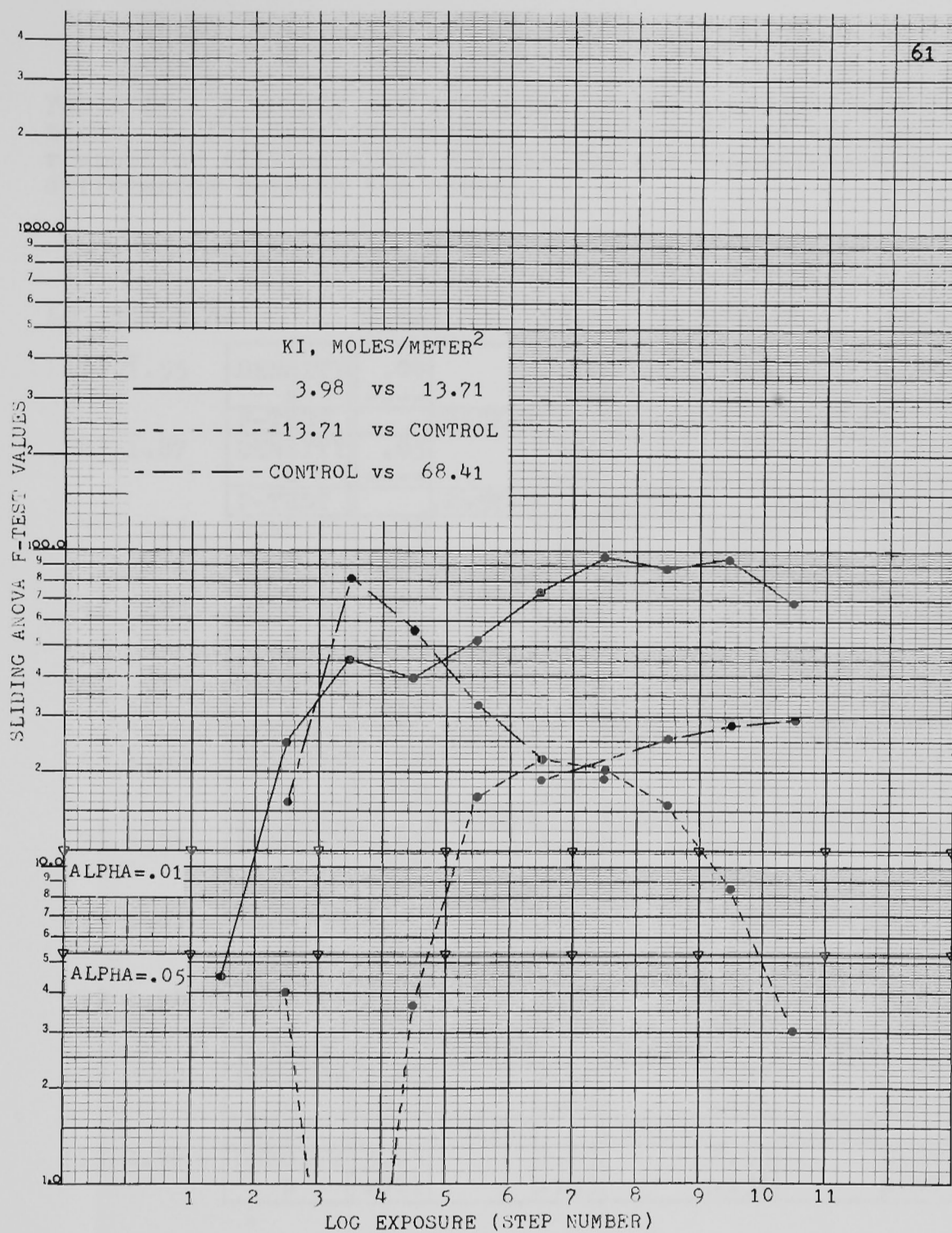


FIGURE 22. Sliding ANOVA F-test values for Figure 21 versus the number of the log exposure step (from Table 13).

TABLE 13. Averages and estimates of the standard deviations, s , for density readings in Figure 21 and the corresponding sliding ANOVA F-tests for the significance of differences between the curves.

		AMOUNTS OF TRANSFERRED IODIDE X 10^{-4} (moles per meter ²)					
LOG EXPOSURE		3.98	13.71	CONTROL	68.41		
1) $\bar{1.55}$	DENSITY	.04	.04	.04	.04	.04	.04
	s	-----	-----	-----	-----	-----	-----
	F-TEST		.450E+1	-----	-----	-----	-----
2) $\bar{1.87}$	DENSITY	.05	.04	.04	.04	.04	.04
	s	-----	-----	-----	-----	-----	-----
	F-TEST		.245E+2	.400E+1	.160E+2		
3) .15	DENSITY	.09	.07	.08	.05	.05	.05
	s	.000	.000	.006	.010	.010	.010
	F-TEST		.451E+2	.668E+0	.807E+2		
4) .43	DENSITY	.20	.15	.15	.11	.11	.11
	s	.010	.012	.006	.006	.006	.006
	F-TEST		.393E+2	.360E+1	.557E+2		
5) .73	DENSITY	.46	.36	.32	.25	.25	.25
	s	.027	.025	.023	.012	.012	.012
	F-TEST		.520E+2	.165E+2	.325E+2		
6) 1.00	DENSITY	.88	.72	.61	.51	.51	.51
	s	.040	.029	.044	.010	.010	.010
	F-TEST		.738E+2	.215E+2	.189E+2		
7) 1.31	DENSITY	1.43	1.17	1.01	.89	.89	.89
	s	.053	.044	.071	.025	.025	.025
	F-TEST		.963E+2	.202E+2	.191E+2		
8) 1.61	DENSITY	1.97	1.65	1.48	1.31	1.31	1.31
	s	.061	.046	.081	.040	.040	.040
	F-TEST		.884E+2	.156E+2	.256E+2		
9) 1.90	DENSITY	2.43	2.08	1.90	1.68	1.68	1.68
	s	.072	.070	.097	.035	.035	.035
	F-TEST		.939E+2	.846E+1	.280E+2		
10) 2.20	DENSITY	2.82	2.40	2.27	1.99	1.99	1.99
	s	.055	.081	.116	.049	.049	.049
	F-TEST		.682E+2	.300E+1	.293E+2		
11) 2.48	DENSITY	3.05	2.63	2.53	2.20	2.20	2.20
	s	.061	.133	.131	.067	.067	.067

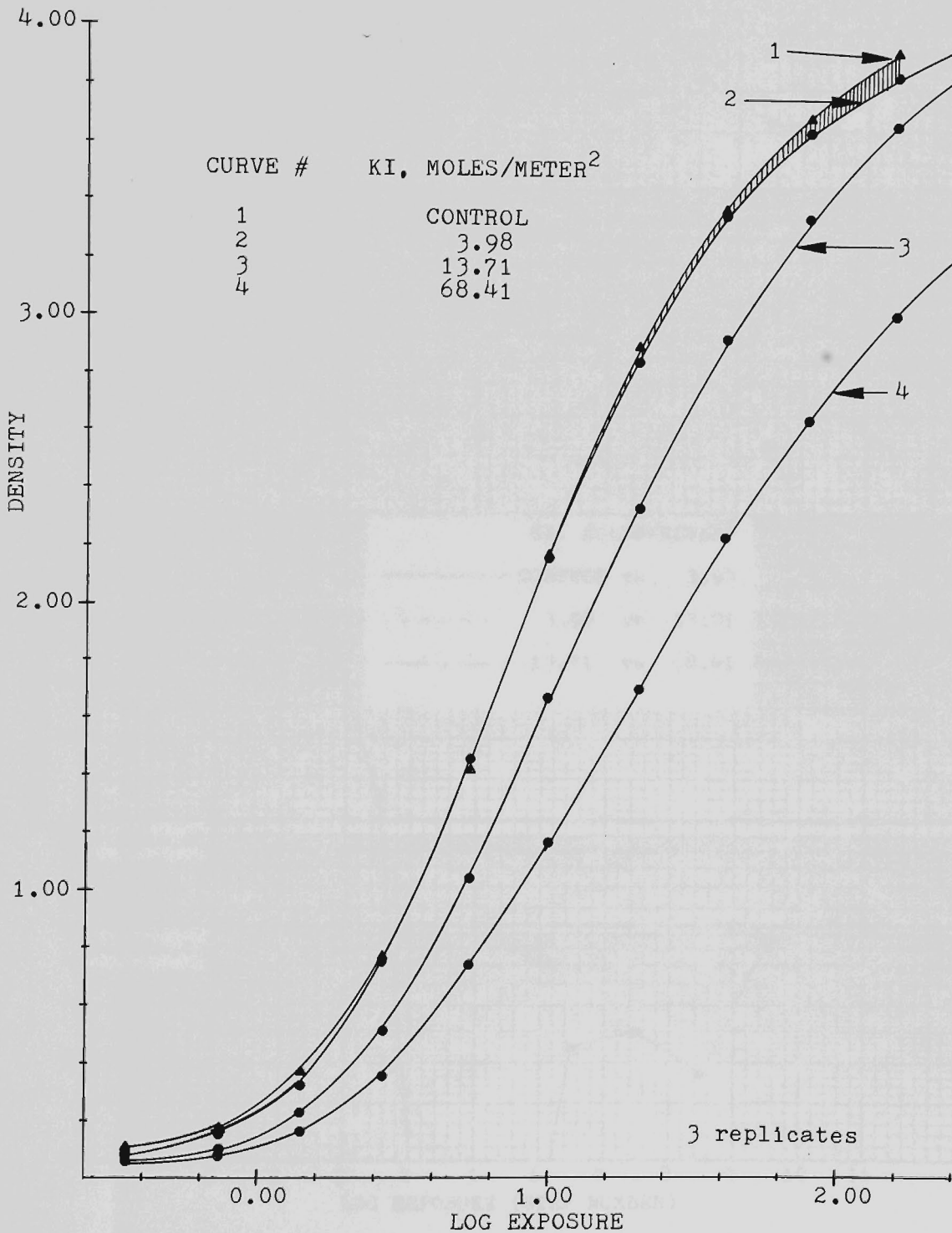


FIGURE 23. Potassium iodide transfer series for Cine Positive Film developed in H₂O developer for ten minutes at 72° Fahrenheit (nitrogen burst agitation).

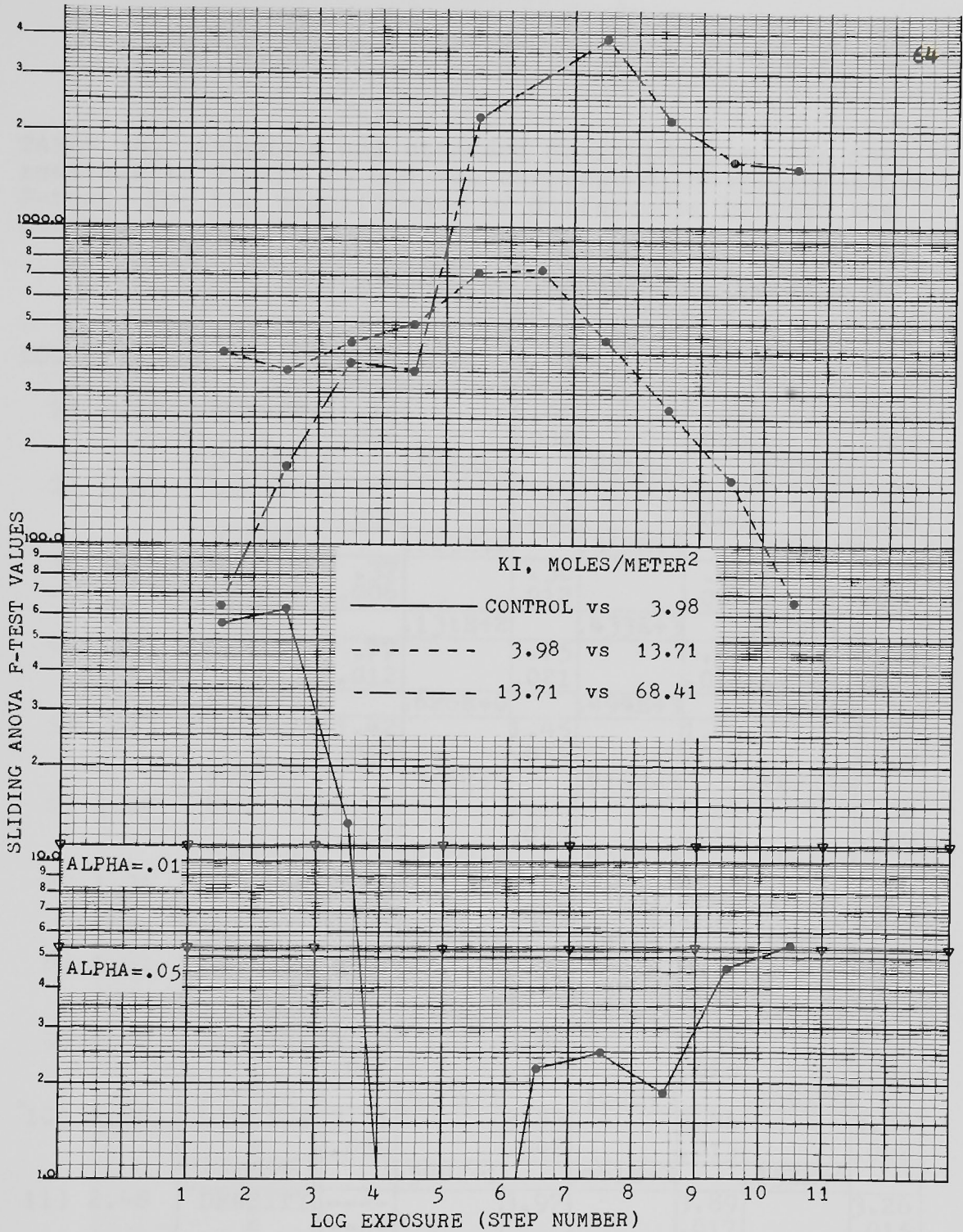


FIGURE 24. Sliding ANOVA F-test values for Figure 23 versus the number of the log exposure step (from Table 14).

TABLE 14. Averages and standard deviations, s, for density readings in Figure 23 and the corresponding sliding ANOVA F-tests for the significance of differences between the curves.

		AMOUNTS OF TRANSFERRED IODIDE X 10 ⁻⁴ (moles per meter ²)							
LOG EXPOSURE		CONTROL		3.98		13.71		68.41	
1) 1.55	DENSITY	.11		.09		.07		.06	
	s	.006		.000		.000		.000	
	F-TEST		.564E+2		.401E+3		.640E+2		
2) 1.87	DENSITY	.17		.15		.10		.08	
	s	.006		.006		.000		.006	
	F-TEST		.629E+2		.352E+3		.176E+3		
3) .15	DENSITY	.37		.32		.22		.16	
	s	.006		.012		.006		.006	
	F-TEST		.131E+2		.433E+3		.374E+3		
4) .43	DENSITY	.77		.75		.51		.25	
	s	.012		.021		.015		.006	
	F-TEST		.626E+0		.494E+3		.350E+3		
5) .73	DENSITY	1.42		1.45		1.04		.74	
	s	.012		.035		.027		.029	
	F-TEST		.556E+0		.716E+3		.122E+4		
6) 1.00	DENSITY	2.17		2.16		1.67		1.16	
	s	.021		.038		.010		.000	
	F-TEST		.220E+1		.731E+3		.184E+5		
7) 1.31	DENSITY	2.89		2.84		2.33		1.70	
	s	.025		.049		.012		.000	
	F-TEST		.248E+1		.441E+3		.383E+4		
8) 1.61	DENSITY	3.37		3.35		2.92		2.23	
	s	.025		.058		.006		.035	
	F-TEST		.185E+1		.268E+3		.215E+4		
9) 1.90	DENSITY	3.69		3.64		3.34		2.64	
	s	.042		.047		.020		.032	
	F-TEST		.459E+1		.160E+3		.160E+4		
10) 2.20	DENSITY	3.91		3.83		3.66		3.00	
	s	.059		.042		.015		.042	
	F-TEST		.540E+1		.661E+2		.152E+4		
11) 2.48	DENSITY	----		3.97		3.89		3.26	
	s	----				.017		.015	

image for silver per unit area of film is by X-ray fluorescence analysis. Unfortunately, X-ray fluorescence analysis equipment which was available for use required a film format with density patches at least one centimeter wide. X-ray fluorescence analysis was therefore not obtainable with exposures made through a Kodak #2 Step Tablet. The question of whether or not the brown tone indicates changes in covering power due to incomplete development remains unanswered.

At the longer H₂Q development time of ten minutes (Figure 23), no increase in density for a given exposure was produced for any of the three amounts of iodide which were transferred. In spite of the acceleration of development in the first three minutes, there was no increase in density produced on full development of a given exposure. The tone of the images was observed to be more nearly neutral or black in appearance for all Cine Positive controls and test strips developed for ten minutes in the H₂Q developer compared to the three minute development. This could be explained by the fact that as development goes towards completion, original iodide in the emulsion is released from the emulsion grains and retards physical development. Consequently, it might be expected that the developed silver would become filamentary in structure and therefore more neutral in tone for longer development

times.

At this point, two types of developers had been used in producing iodide transfer series with Cine Positive 5302 film. Iodide in low amounts produced development acceleration with the hydroquinone developer (H_2Q) and only retardation with the DK-50 formulation. These different results for the two types of developers had been reported earlier by Sheppard and Meyer³⁰ (they failed to base their results on mass of developed silver versus exposure, so their data is also susceptible to unaccounted for changes in covering power). The H_2Q developer had a pH of approximately 10.61, whereas the DK-50 developer had a pH of approximately 9.58. To demonstrate that the lack of acceleration with the DK-50 developer was not attributable to its lower pH (pH = 9.58) as compared to that of H_2Q developer (with a pH of 10.60), the DK-50* developer with an elevated pH of 10.67 was used to produce iodide transfer series (the developer formulations are listed in Table 1).

The results of the iodide transfer series using Cine Positive 5302 film and DK-50* developer for development times of three and ten minutes are shown in Figure 25 through Figure 28. The values are listed in Table 15 and Table 16. No acceleration was observed. The retardation of development for all three levels of iodide transfer was greater for the DK-50* developer than it was

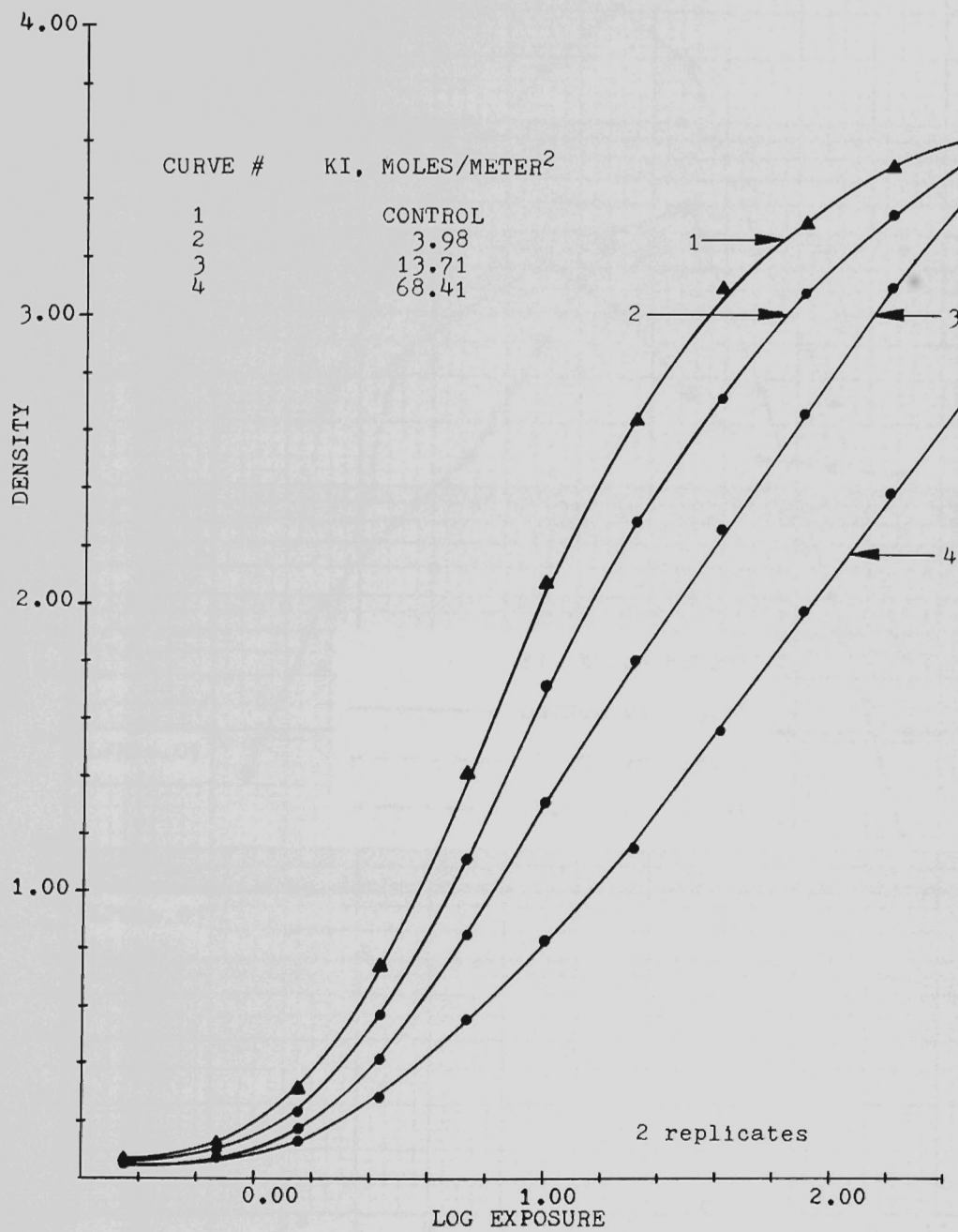


FIGURE 25. Potassium iodide transfer series for Cine Positive film developed in DK-50* for three minutes at 72° Fahrenheit (nitrogen burst agitation).

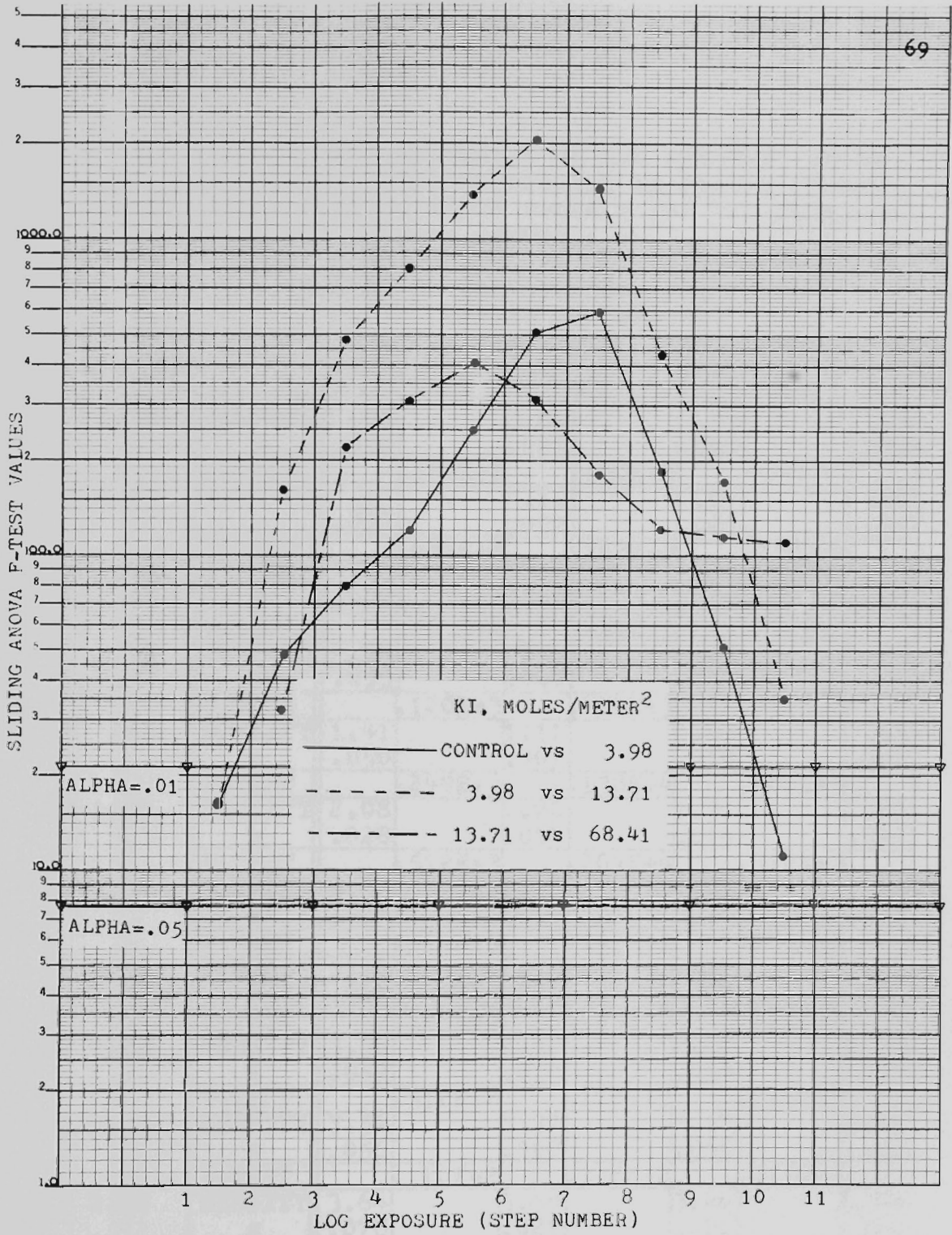


FIGURE 26. Sliding ANOVA F-test values for Figure 25 versus the number of the log exposure step (from Table 15).

TABLE 15. Averages and estimates of the standard deviations, s , for density readings plotted in Figure 25 and the corresponding sliding ANOVA F-tests for the significance of differences between curves.

		AMOUNT OF TRANSFERRED IODIDE X 10^{-4} (moles per meter ²)						
LOG EXPOSURE		CONTROL	3.98	13.71	68.41			
1) $\bar{1}.55$	DENSITY	.07		.06		.05		.06
	s	.000		.007		.000		.000
	F-TEST		.163E+2		.160E+2		-----	
2) $\bar{1}.87$	DENSITY	.13		.10		.07		.07
	s	.007		.007		.007		.000
	F-TEST		.481E+2		.162E+3		.320E+2	
3) .15	DENSITY	.31		.23		.17		.13
	s	.021		.000		.000		.007
	F-TEST		.795E+2		.481E+3		.218E+3	
4) .43	DENSITY	.74		.57		.41		.28
	s	.035		.000		.014		.000
	F-TEST		.120E+3		.804E+3		.308E+3	
5) .73	DENSITY	1.41		1.11		.85		.55
	s	.050		.007		.014		.028
	F-TEST		.249E+3		.138E+4		.406E+3	
6) 1.00	DENSITY	2.08		1.72		1.31		.83
	s	.028		.014		.014		.042
	F-TEST		.512E+3		.204E+4		.312E+3	
7) 1.31	DENSITY	2.65		2.30		1.81		1.15
	s	.028		.014		.014		.078
	F-TEST		.590E+3		.145E+4		.180E+3	
8) 1.61	DENSITY	3.11		2.73		2.27		1.56
	s	.007		.028		.007		.120
	F-TEST		.185E+3		.435E+3		.121E+3	
9) 1.90	DENSITY	3.34		3.10		2.68		1.98
	s	.057		.014		.050		.127
	F-TEST		.512E+2		.172E+3		.114E+3	
10) 2.20	DENSITY	3.54		3.37		3.12		2.40
	s	.056		.000		.050		.120
	F-TEST		.110E+2		.348E+2		.110E+3	
11) 2.48	DENSITY	3.64		3.58		3.46		2.78
	s	.078		.021		.071		.127

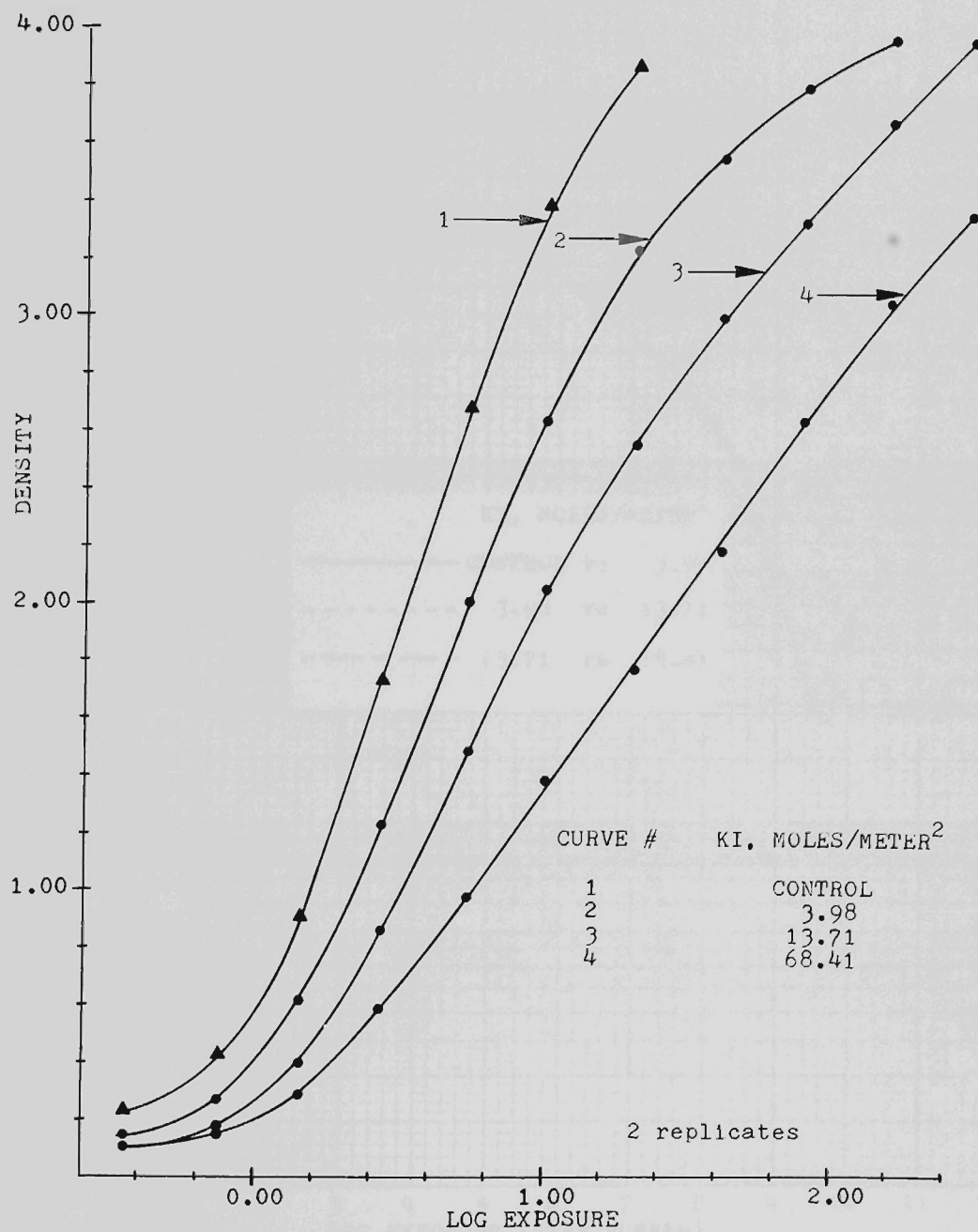


FIGURE 27. Potassium iodide transfer series for Cine Positive film developed in DK-50* for ten minutes at 72° Fahrenheit (nitrogen burst agitation).

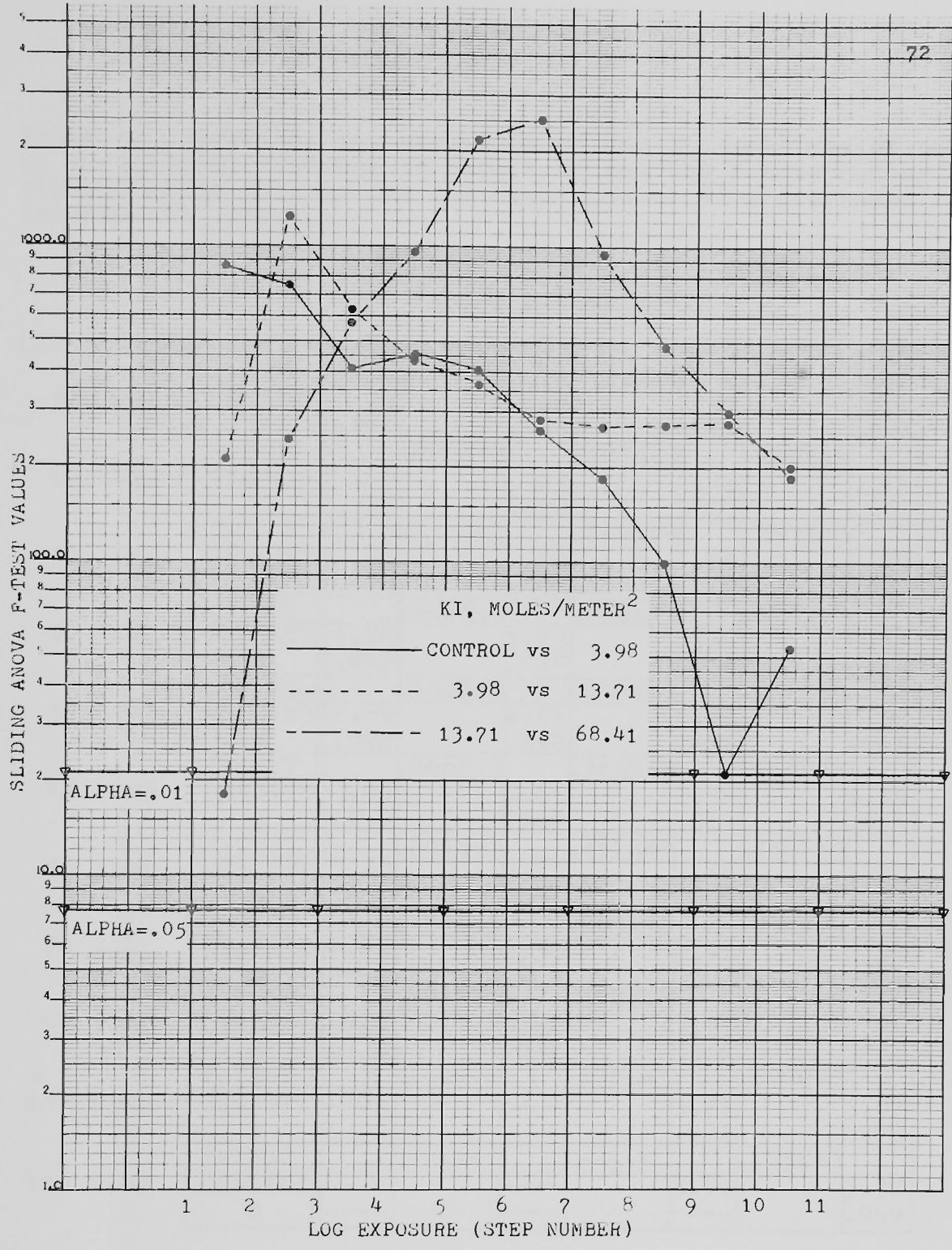


FIGURE 28. Sliding ANOVA F-TEST values for Figure 27 versus the number of the log exposure step (from Table 16).

TABLE 16. Averages and estimates of the standard deviations, s , for density readings in Figure 27 and the corresponding sliding ANOVA F-tests for the significance of differences between the curves.

AMOUNTS OF TRANSFERRED IODIDE $\times 10^{-4}$
(moles per meter²)

LOG EXPOSURE		CONTROL	3.98	13.71	68.41
1) $\bar{1}.55$	DENSITY	.24	.15	.11	.11
	s	.007	.007	.007	.007
2) $\bar{1}.87$	F-TEST	.866E+3	.209E+3	.180E+2	
	DENSITY	.43	.27	.18	.16
3) .15	s	.007	.000	.007	.007
	F-TEST	.752E+3	.123E+4	.243E+3	
4) .43	DENSITY	.91	.62	.40	.29
	s	.014	.007	.007	.007
5) .73	F-TEST	.412E+3	.633E+3	.578E+3	
	DENSITY	1.74	1.23	.86	.59
6) 1.00	s	.042	.028	.014	.014
	F-TEST	.456E+3	.440E+3	.958E+3	
7) 1.31	DENSITY	2.69	2.01	1.49	.98
	s	.042	.042	.028	.007
8) 1.61	F-TEST	.406E+3	.365E+3	.218E+4	
	DENSITY	3.40	2.65	2.06	1.39
9) 1.90	s	.050	.064	.014	.014
	F-TEST	.261E+3	.281E+3	.252E+4	
10) 2.20	DENSITY	3.89	3.25	2.57	1.78
	s	.035	.085	.007	.035
11) 2.48	F-TEST	.184E+3	.269E+3	.951E+3	
	DENSITY	----	3.57	3.01	2.20
12) 2.48	s	----	.064	.007	.064
	F-TEST	.101E+3	.272E+3	.481E+3	
13) 2.48	DENSITY	----	3.82	3.35	2.65
	s	----	.057	.014	.071
14) 2.48	F-TEST	-----	.276E+3	.299E+3	
	DENSITY	----	----	3.70	3.07
15) 2.48	s	----	----	.021	.078
	F-TEST	-----	-----	.185E+3	
16) 2.48	DENSITY	----	----	3.98	3.37
	s	----	----	----	.099

for DK-50 developer, perhaps because retardation depends on the relative developer activity or completeness of development (DK-50 has the higher activity).

Figure 29 and Figure 30 show Cine Positive contrast index and relative speeds, respectively, for development in the three developers as a function of mole percent of iodide transferred to Cine Positive film. A comparison of the three iodide transfer levels for development with DK-50 (Figure 17) and DK-50* (Figure 25) at three minutes development time indicates a higher relative speed for the DK-50* developer (the DK-50* iodide transfer curves appeared to be shifted approximately .2 log exposure units from that of DK-50 iodide transfer curves along the log exposure axis, giving higher speed). The curve shape and contrast index were essentially the same for the two developers except for the control strips. The DK-50* control strips had a higher contrast index than the corresponding DK-50 control strips. A comparison of the two developers for ten minutes development time showed primarily that DK-50* development produced a higher contrast index than DK-50 for all control and iodide transfer characteristic curves. This is a predictable result because the relatively high pH of the DK-50* causes it to be more active than DK-50.

The contrast index and shapes of the iodide transfer series for DK-50 developer at ten minutes development

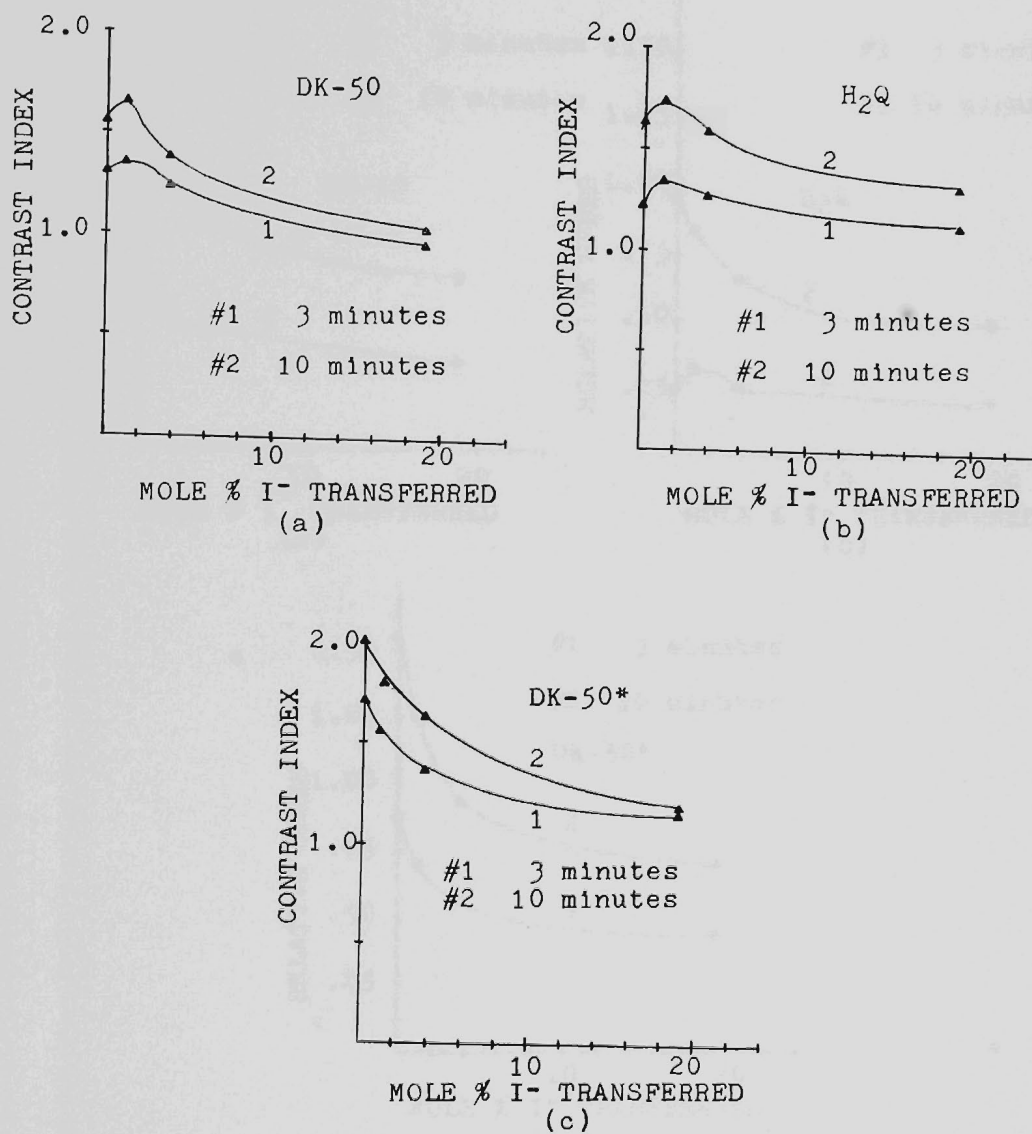


FIGURE 29. Contrast index versus the amount of iodide transferred to Cine Positive 5302 film (expressed in mole percent). Two development times were used with three developers; a) DK-50 developer, b) H₂Q developer, and c) DK-50* developer.

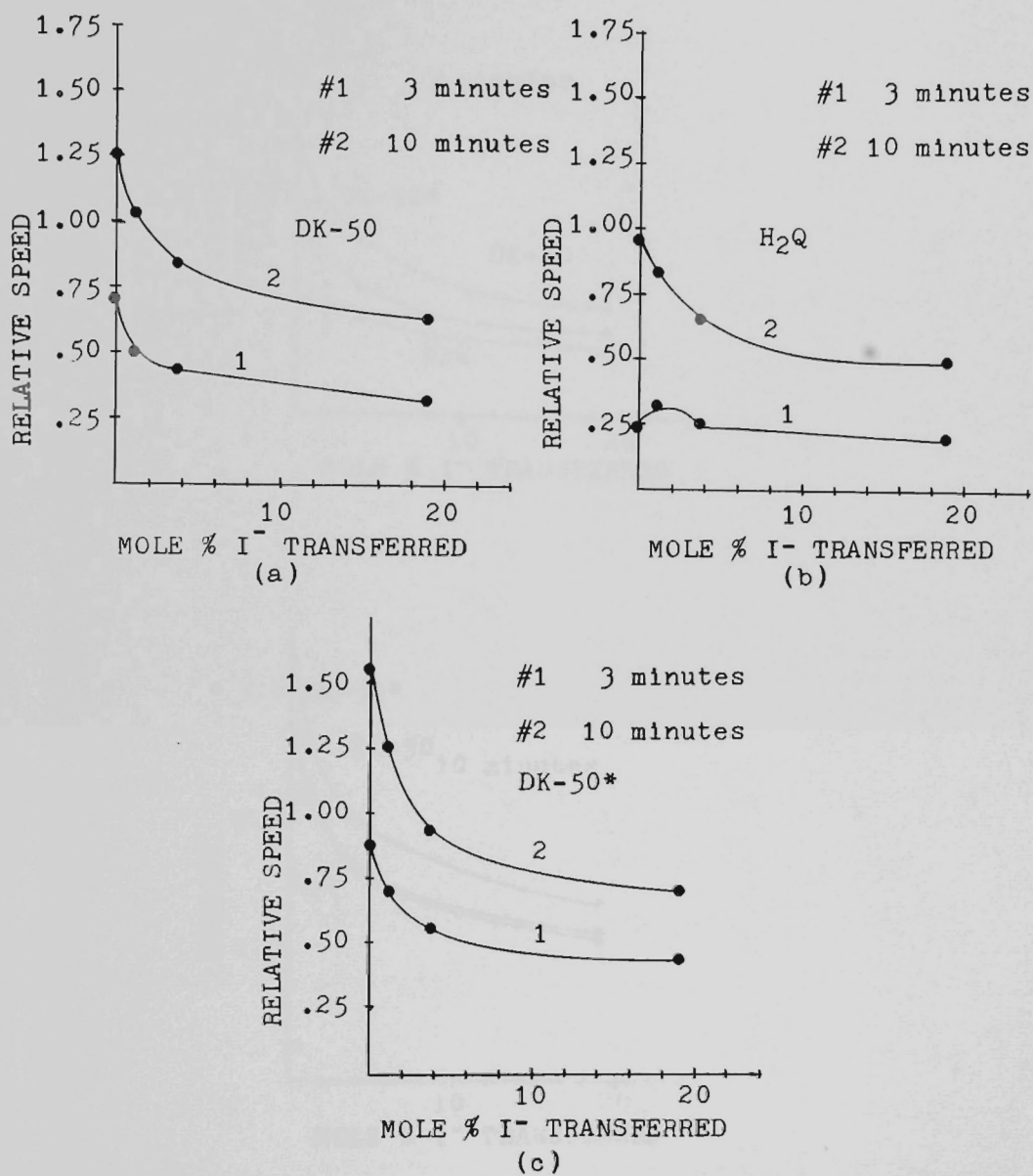


FIGURE 30. Relative speed versus the mole percent of iodide transferred to Cine Positive 5302 film and developed in three different developers for two development times: a) DK-50, b) H₂Q, and c) DK-50*.

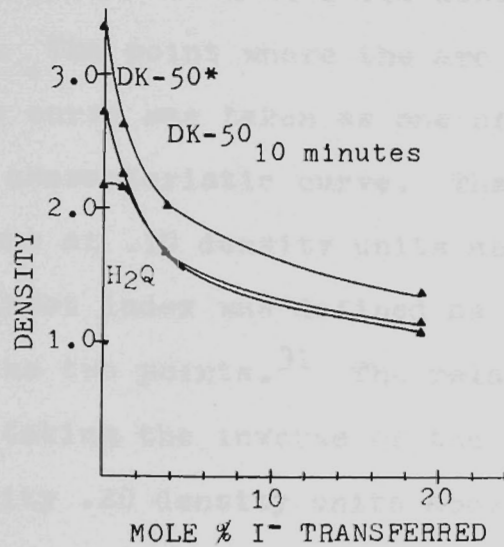
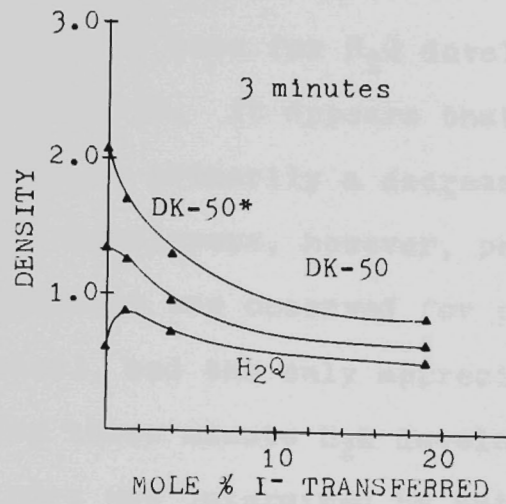


FIGURE 31. Intercomparison of Cine Positive iodide transfer series at one exposure level (log exposure = 1.00) for development with three developers and two times of development.

time are very similar to those obtained with the H₂Q developer. The loss of speed with increasing amounts of transferred iodide is less for H₂Q development than for development with DK-50. It appears that acceleration of H₂Q by iodide may be primarily a decrease in induction period. For all developers, however, permanent retardation of development was observed for prolonged development (ten minutes), and the only appreciable acceleration observed was for three minute H₂Q development.

Contrast index was determined by swinging an arc two log exposure units in diameter about the point on the characteristic curve which lies .10 density units above base plus fog. The point where the arc crossed the characteristic curve was taken as one of a set of two points on the characteristic curve. The other point was the original one at .10 density units above base plus fog. The contrast index was defined as the slope of the line joining the two points.³¹ The relative speed was determined by taking the inverse of the exposure required to give a density .20 density units above base plus fog.

To facilitate intercomparison of the data for each of the three developers, a plot of density (at a log exposure of 1.00) versus mole percent of transferred iodide was prepared (Figure 31). It is evident from the three minute data that the iodide has little or no retarding effect on development by H₂Q developer at these

particular amounts of transferred iodide. There is a definite retardation for development by both DK-50 and DK-50*, however. For the ten minute data, retardation is pronounced for the DK-50 and DK-50* developers, whereas there is considerably less retardation for the two high values of iodide transfer developed in H₂Q and little or no retardation by the low value of iodide transfer.

Cine Positive 5302 film is known to be a relatively simple type of emulsion. For this reason it is often used in photographic science research. It is certainly not typical of present camera films. Therefore, Panatomic X 5060 film (Pan X) was used for further iodide transfer analysis because it was believed to be more representative of modern camera films.

The results of the Pan X iodide transfer series using the three developers are found in Figure 32 through Figure 47, and Table 17 through Table 24. Only retardation of development was observed for all levels of iodide with DK-50 and DK-50* as the developers as was the case for Cine Positive 5302 film. A series of iodide transfers to Pan X was accomplished for a development time of two minutes in DK-50 to see if acceleration occurred at the shorter development time (Figure 32 and Table 17). The evidence indicates otherwise.

For iodide transferred to Panatomic X and developed in the H₂Q developer, rather unexpected results were

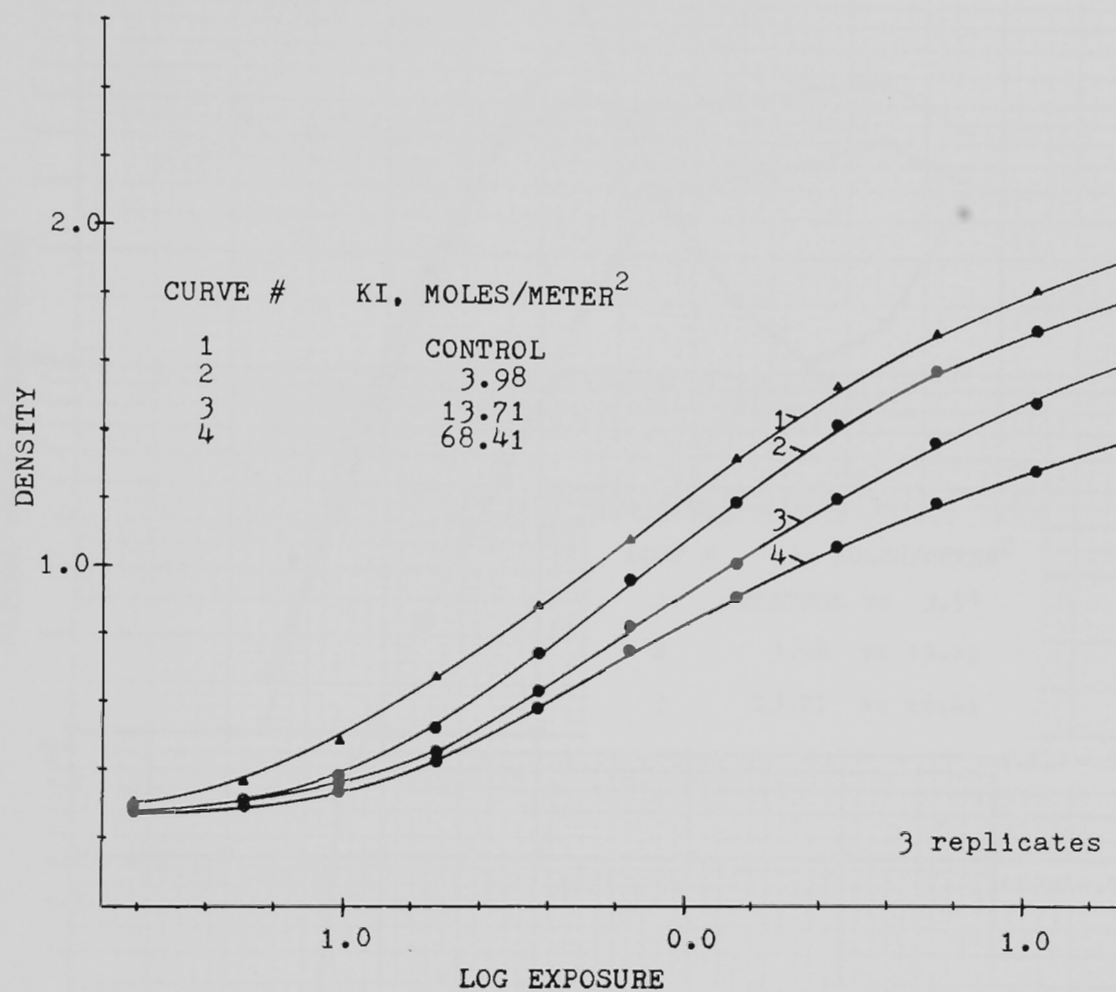


FIGURE 32. Potassium iodide transfer series for Panatomic X film developed in DK-50 for two minutes at 72° Fahrenheit (nitrogen burst agitation).

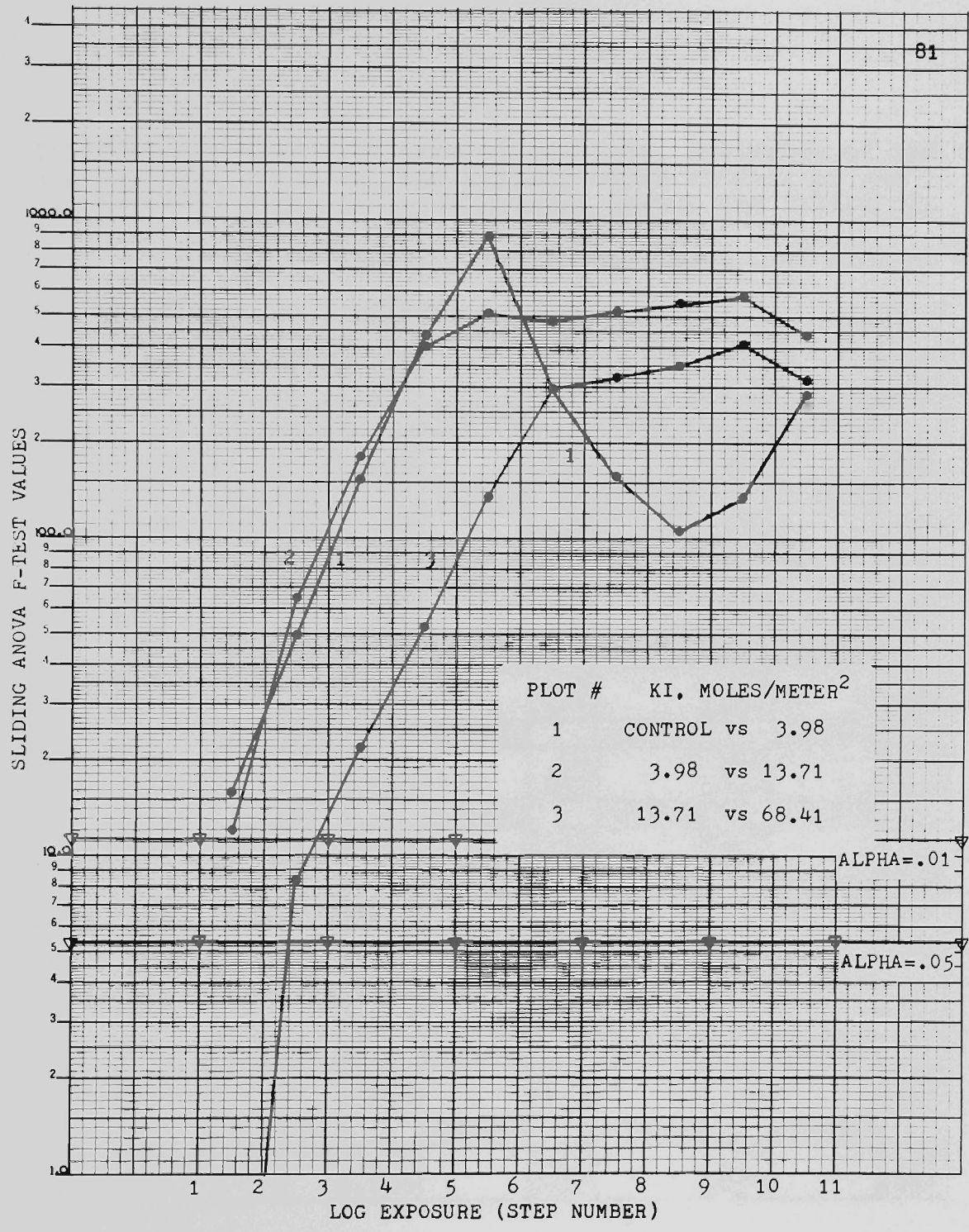


FIGURE 33. Sliding ANOVA F-test values for Figure 32 versus the number of the log exposure step (from Table 17).

TABLE 17. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 32.

AMOUNT OF IODIDE TRANSFERRED X 10^{-4} (moles/meter²)

LOG EXPOSURE		CONTROL	3.98	13.71	68.41
1) $\bar{2}.39$	DENSITY	.30	.28	.27	.27
	s	.017	.000	.006	.006
	F-TEST	.156E+2	.120E+2	.326E 0	
2) $\bar{2}.71$	DENSITY	.36	.31	.29	.29
	s	.026	.000	.025	.000
	F-TEST	.490E+2	.653E+2	.830E+2	
3) $\bar{2}.99$	DENSITY	.49	.38	.35	.33
	s	.029	.000	.006	.006
	F-TEST	.152E+3	.180E+3	.218E+2	
4) $\bar{1}.27$	DENSITY	.67	.52	.45	.42
	s	.021	.000	.012	.010
	F-TEST	.460E+3	.401E+3	.523E+2	
5) $\bar{1}.57$	DENSITY	.88	.74	.63	.58
	s	.010	.000	.010	.006
	F-TEST	.878E+3	.509E+3	.135E+3	
6) $\bar{1}.84$	DENSITY	1.08	.96	.82	.75
	s	.000	.012	.012	.006
	F-TEST	.296E+3	.483E+3	.299E+3	
7) .15	DENSITY	1.31	1.19	1.01	.91
	s	.015	.015	.012	.000
	F-TEST	.155E+3	.520E+3	.323E+3	
8) .45	DENSITY	1.53	1.41	1.20	1.06
	s	.020	.015	.017	.012
	F-TEST	.104E+3	.551E+3	.348E+3	
9) .74	DENSITY	1.69	1.58	1.37	1.19
	s	.025	.015	.015	.015
	F-TEST	.135E+3	.574E+3	.411E+3	
10) 1.04	DENSITY	1.82	1.69	1.49	1.29
	s	.015	.012	.017	.017
	F-TEST	.283E+3	.436E+3	.316E+3	
11) 1.32	DENSITY	1.91	1.80	1.60	1.39
	s	.006	.015	.021	.021

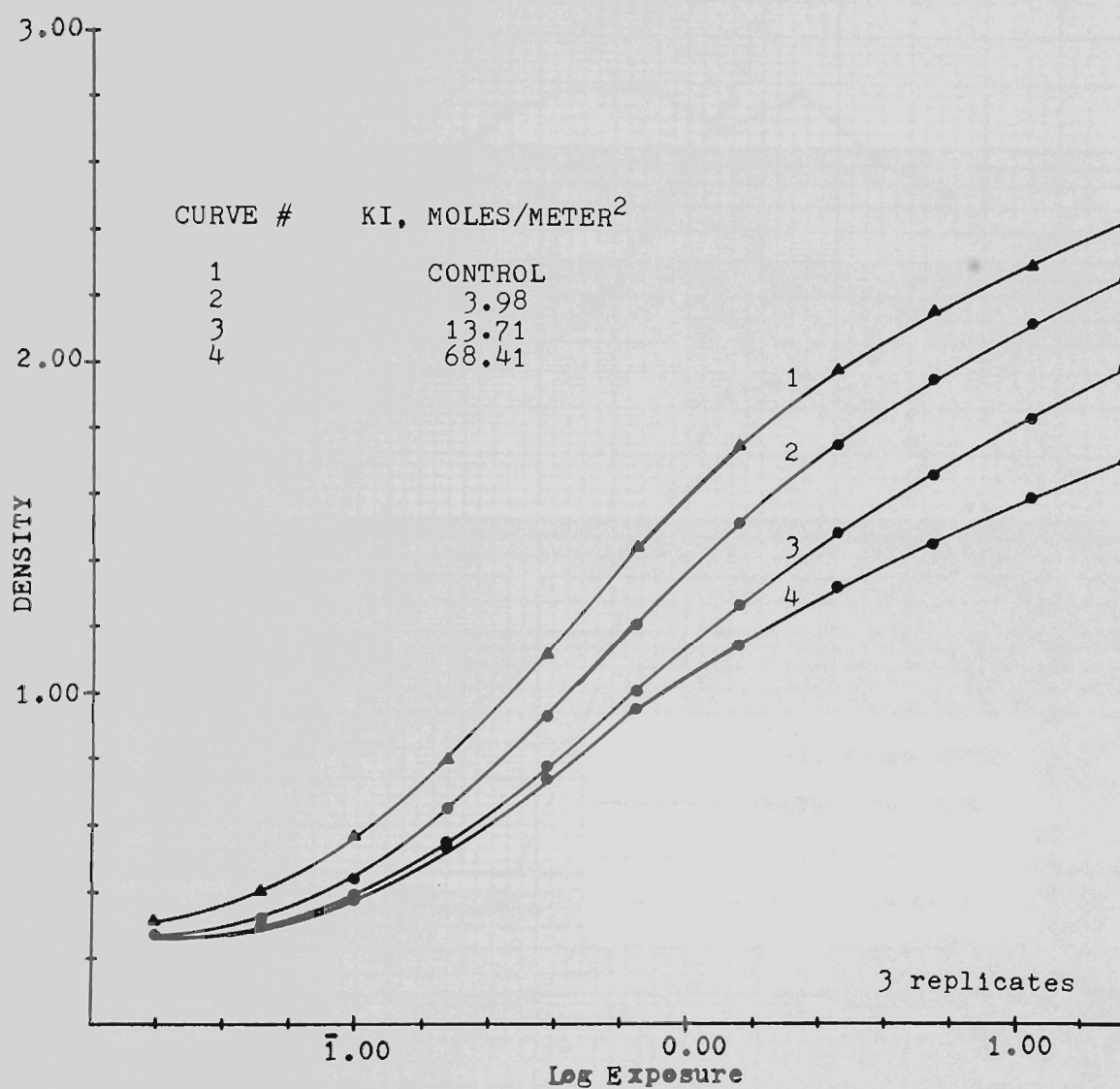


FIGURE 34. Potassium iodide transfer series for Panatomic X film developed in DK-50 for three minutes at 72° Fahrenheit (nitrogen burst agitation).

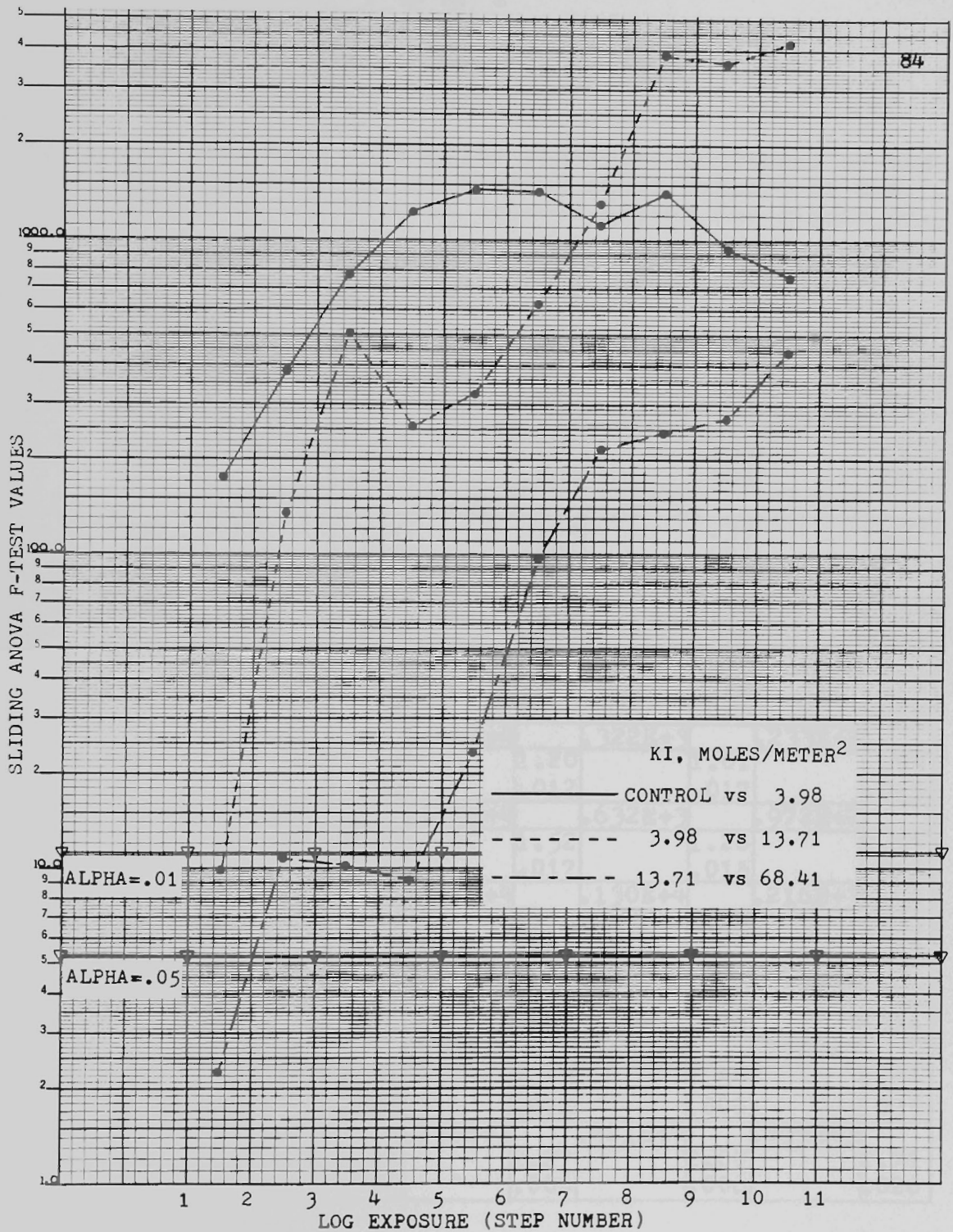


FIGURE 35. Sliding ANOVA F-test values for Figure 34 versus the number of the log exposure step (from Table 18).

TABLE 18. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-TESTS of the significance of differences between curves for Figure 34.

		AMOUNT OF IODIDE TRANSFERRED X 10^{-4} (moles/meter ²)							
LOG EXPOSURE		CONTROL	3.98	13.71	68.41				
1) $\bar{2}.39$	DENSITY	.31		.27		.26		.26	
	s	.006		.010		.006		.006	
	F-TEST		.175E+3		.981E+1		.225E+1		
2) $\bar{2}.71$	DENSITY	.40		.32		.30		.29	
	s	.010		.000		.006		.006	
	F-TEST		.384E+3		.134E+3		.107E+2		
3) $\bar{2}.99$	DENSITY	.57		.44		.39		.37	
	s	.015		.006		.006		.010	
	F-TEST		.772E+3		.502E+3		.101E+2		
4) $\bar{1}.27$	DENSITY	.80		.65		.55		.53	
	s	.006		.006		.006		.015	
	F-TEST		.122E+4		.255E+3		.912E+1		
5) $\bar{1}.57$	DENSITY	1.12		.93		.78		.74	
	s	.000		.015		.023		.015	
	F-TEST		.144E+4		.322E+3		.233E+2		
6) $\bar{1}.84$	DENSITY	1.45		1.20		1.01		.95	
	s	.006		.012		.017		.015	
	F-TEST		.142E+4		.632E+3		.972E+2		
7) .15	DENSITY	1.76		1.52		1.26		1.15	
	s	.006		.017		.015		.015	
	F-TEST		.111E+4		.130E+4		.216E+3		
8) .45	DENSITY	1.99		1.76		1.49		1.33	
	s	.015		.006		.010		.023	
	F-TEST		.141E+4		.385E+4		.243E+3		
9) .74	DENSITY	2.17		1.96		1.67		1.46	
	s	.012		.006		.010		.026	
	F-TEST		.938E+3		.363E+4		.270E+3		
10) 1.04	DENSITY	2.31		2.13		1.84		1.59	
	s	.015		.012		.006		.035	
	F-TEST		.758E+3		.421E+4		.439E+3		
11) 1.32	DENSITY	2.44		2.27		2.00		1.71	
	s	.012		.006		.006		.026	

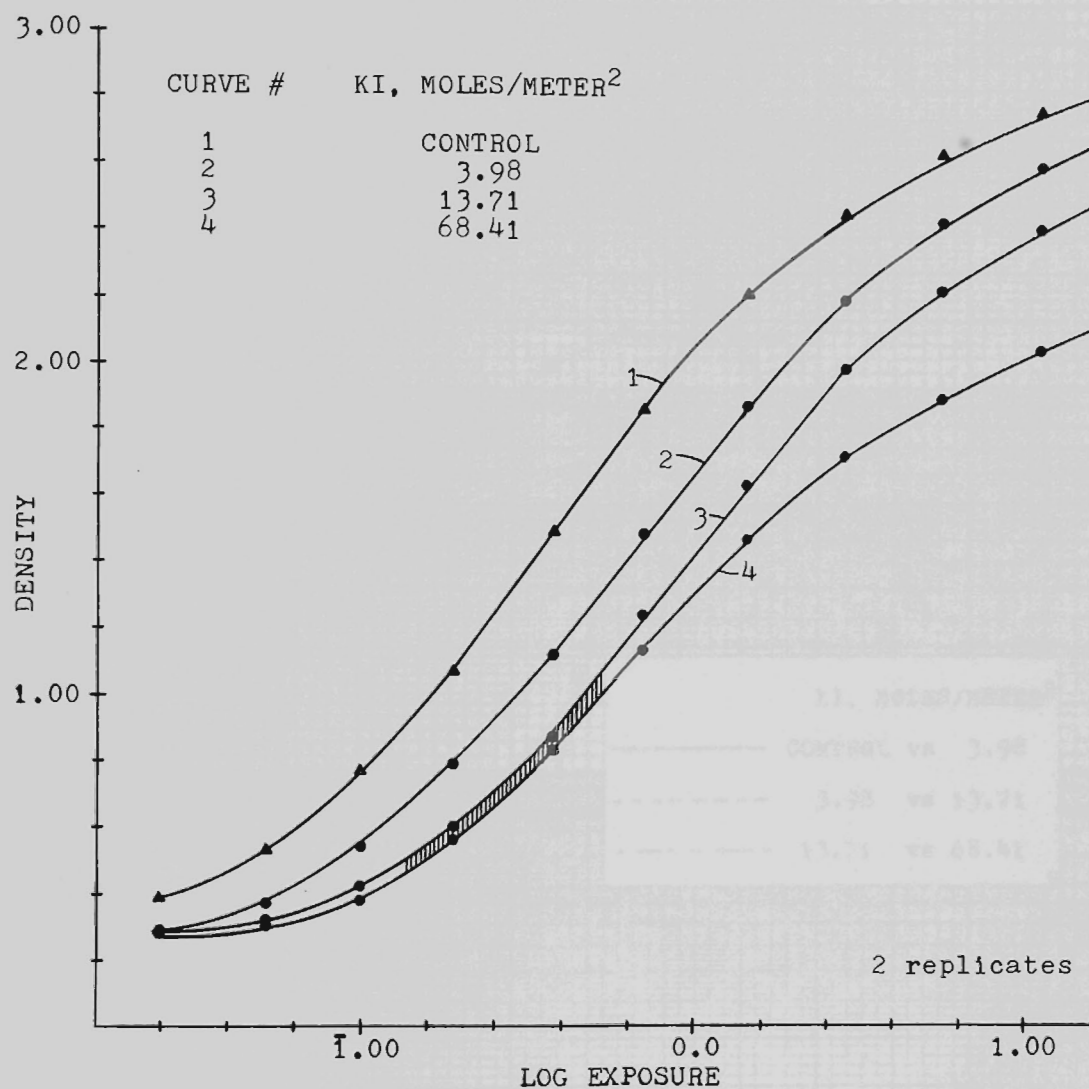


FIGURE 36. Potassium iodide transfer series for Panatomic X film developed in DK-50 for ten minutes at 72° Fahrenheit (nitrogen burst agitation).

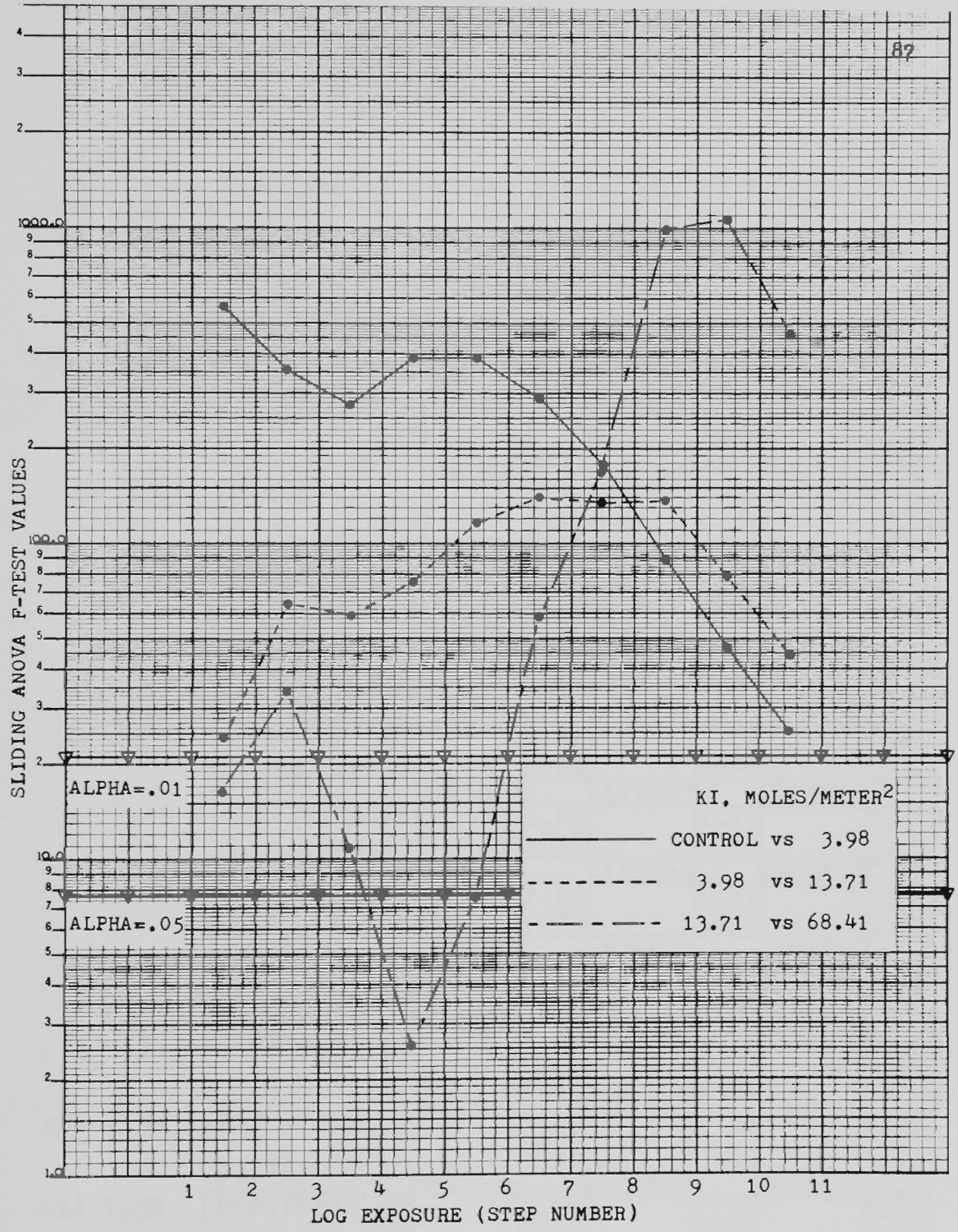


FIGURE 37. Sliding ANOVA F-test values for Figure 36 versus the number of the log exposure step (from Table 19).

TABLE 19. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 36.

		AMOUNT OF IODIDE TRANSFERRED X 10^{-4} (moles/meter ²)			
LOG EXPOSURE		CONTROL	3.98	13.71	68.41
1) $\bar{2}.39$	DENSITY	.39	.29	.28	.27
	s	.000	.000	.000	.000
2) $\bar{2}.71$	F-TEST	.562E+3	.242E+2	.163E+2	
	DENSITY	.53	.37	.32	.29
3) $\bar{2}.99$	s	.007	.014	.000	.007
	F-TEST	.356E+3	.641E+2	.337E+2	
4) $\bar{1}.27$	DENSITY	.77	.53	.42	.38
	s	.014	.021	.014	.007
5) $\bar{1}.57$	F-TEST	.274E+3	.590E+2	.108E+2	
	DENSITY	1.07	.79	.60	.55
6) $\bar{1}.84$	s	.000	.035	.035	.007
	F-TEST	.386E+3	.750E+2	.256E+1	
7) .15	DENSITY	1.49	1.12	.86	.83
	s	.021	.021	.042	.035
8) .45	F-TEST	.385E+3	.116E+3	.751E+1	
	DENSITY	1.86	1.48	1.23	1.13
9) .74	s	.035	.028	.028	.000
	F-TEST	.289E+3	.140E+3	.583E+2	
10) 1.04	DENSITY	2.21	1.86	1.63	1.46
	s	.021	.035	.021	.035
11) 1.32	F-TEST	.178E+3	.134E+3	.169E+3	
	DENSITY	2.45	2.19	1.98	1.72
12) 1.61	s	.035	.035	.000	.021
	F-TEST	.889E+2	.136E+3	.992E+3	
13) 1.89	DENSITY	2.63	2.42	2.22	1.89
	s	.035	.035	.007	.014
14) 2.18	F-TEST	.469E+2	.786E+2	.106E+4	
	DENSITY	2.76	2.59	2.39	2.04
15) 2.47	s	.028	.049	.021	.014
	F-TEST	.251E+2	.438E+2	.463E+3	
16) 2.76	DENSITY	2.84	2.71	2.53	2.15
	s	.028	.049	.035	.021

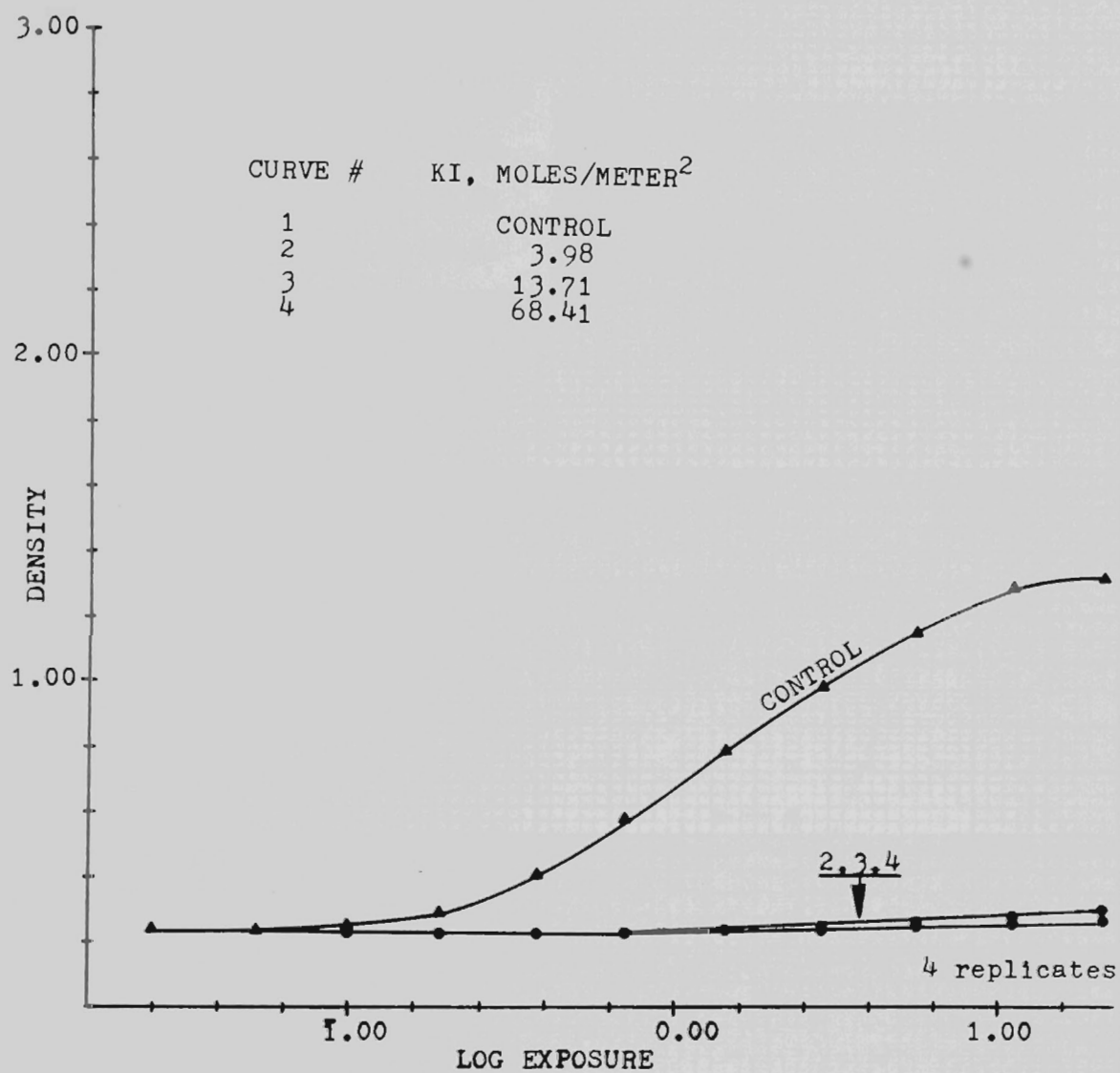


FIGURE 38. Potassium iodide transfer series for Panatomic X film developed in H_2O for three minutes at 72° Fahrenheit (nitrogen burst agitation).

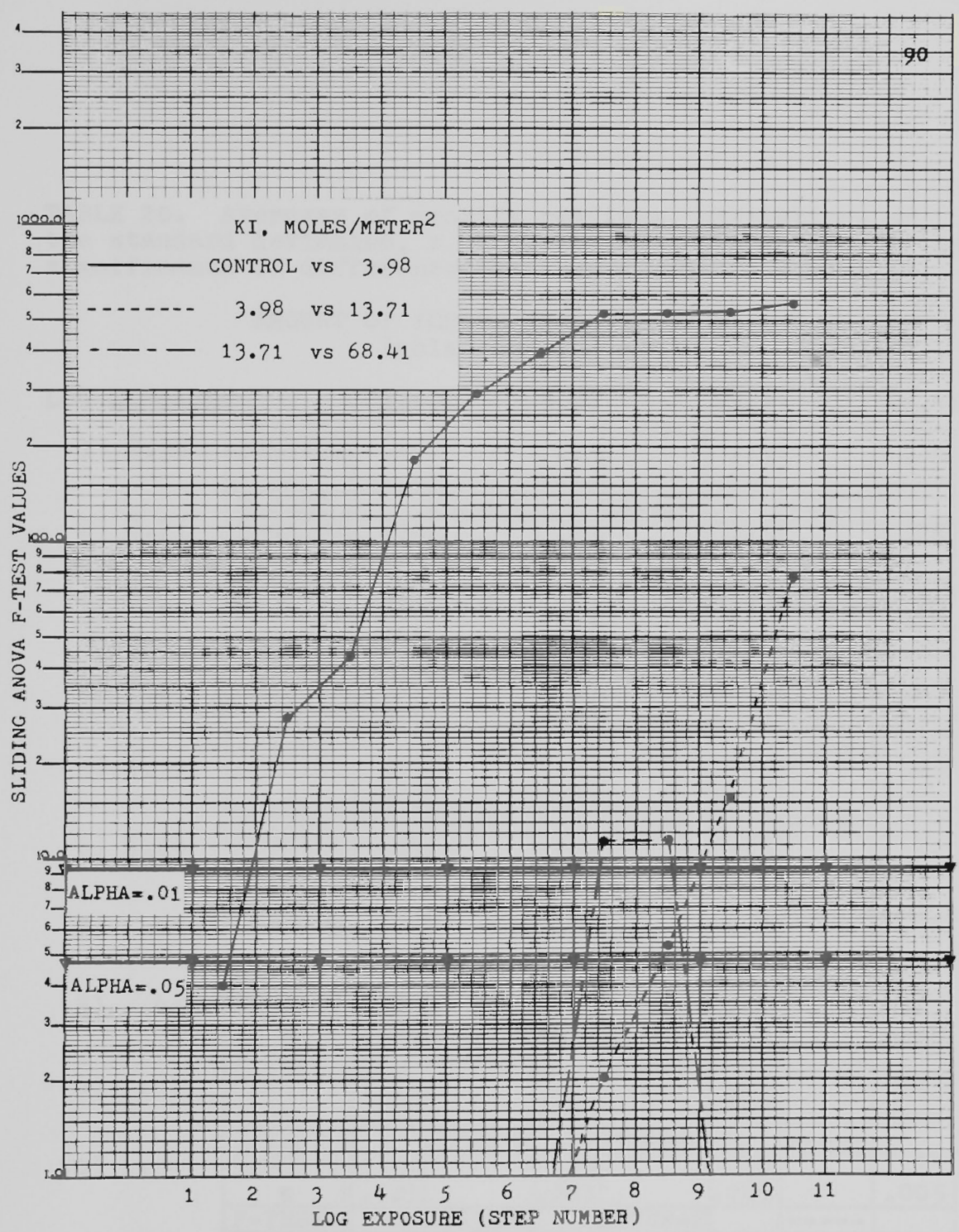


FIGURE 39. Sliding ANOVA F-test values for Figure 38 versus the number of the log exposure step (from Table 20).

TABLE 20. Averages of density readings, estimations of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves in Figure 38.

		AMOUNT OF IODIDE TRANSFERRED X 10 ⁻⁴ (moles/meter ²)			
LOG EXPOSURE		CONTROL	3.98	13.71	68.41
1) $\bar{2}.39$	DENSITY	.24	.23	.23	.24
	s	-----	-----	-----	-----
	F-TEST	-----	-----	-----	-----
2) $\bar{2}.71$	DENSITY	.24	.23	.23	.24
	s	-----	-----	-----	-----
	F-TEST	-----	-----	-----	-----
3) $\bar{2}.99$	DENSITY	.25	.23	.23	.24
	s	.006	-----	-----	-----
	F-TEST	-----	-----	-----	-----
4) $\bar{1}.27$	DENSITY	.29	.23	.23	.24
	s	.028	-----	-----	-----
	F-TEST	-----	-----	-----	-----
5) $\bar{1}.57$	DENSITY	.41	.23	.23	.24
	s	.025	-----	-----	-----
	F-TEST	-----	-----	-----	-----
6) $\bar{1}.84$	DENSITY	.58	.23	.23	.24
	s	.054	-----	-----	-----
	F-TEST	-----	-----	-----	-----
7) .15	DENSITY	.79	.24	.23	.24
	s	.072	-----	-----	-----
	F-TEST	-----	-----	-----	-----
8) .45	DENSITY	.99	.25	.24	.25
	s	.086	-----	-----	-----
	F-TEST	.525E+3	.532E+1	-----	-----
9) .74	DENSITY	1.16	.26	.25	.25
	s	.113	.010	.005	-----
	F-TEST	.532E+3	.154E+2	-----	-----
10) 1.04	DENSITY	1.30	.28	.26	.26
	s	.121	.011	.005	.005
	F-TEST	.563E+3	.778E+2	-----	-----
11) 1.32	DENSITY	1.33	.30	.27	.27
	s	.123	.000	.000	.000

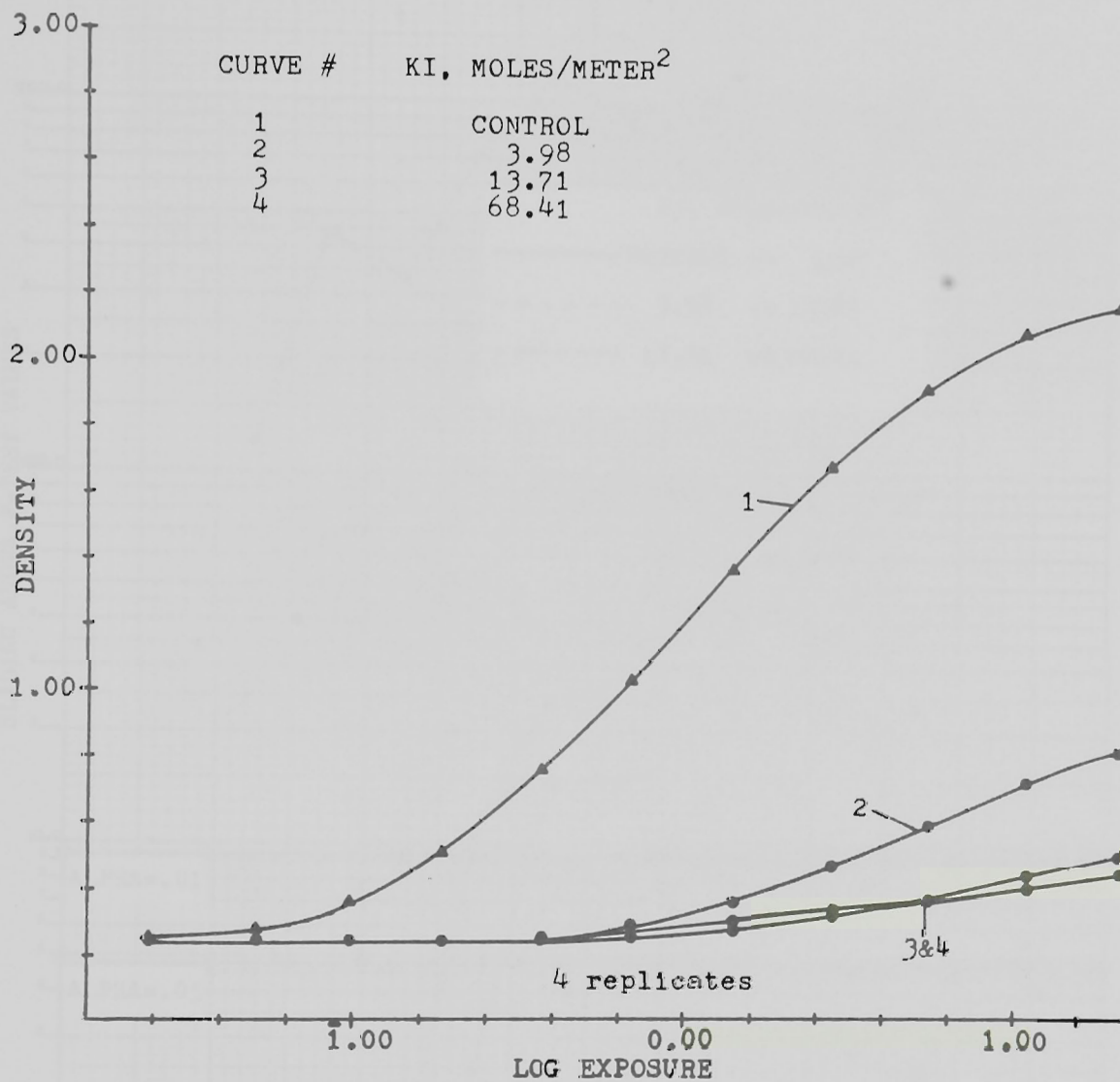


FIGURE 40. Potassium iodide transfer series for Panatomic X film developed in H_2O for five minutes at 72° Fahrenheit (nitrogen burst agitation).

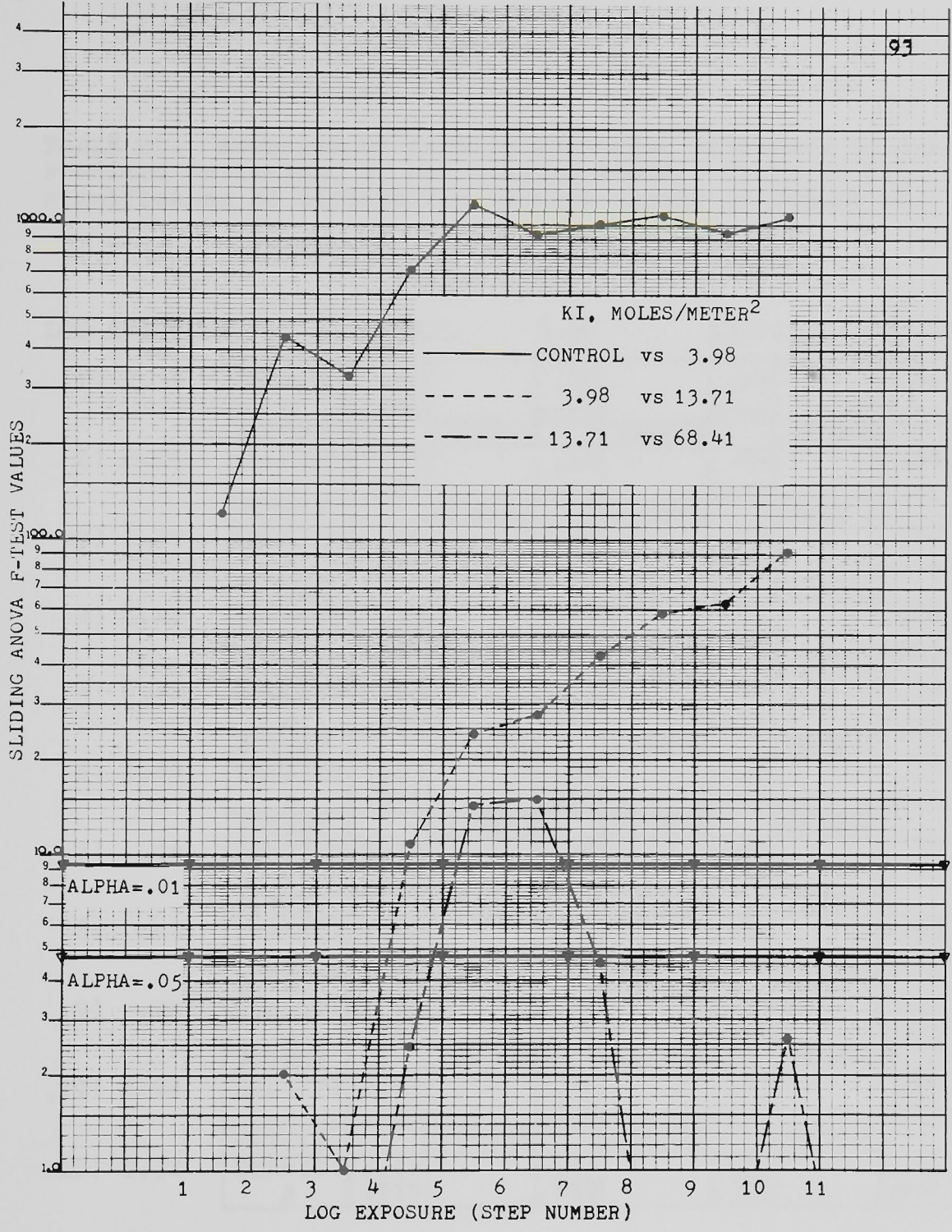


FIGURE 41. Sliding ANOVA F-test values for Figure 40 versus the number of the log exposure step (from Table 21).

TABLE 21. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves in Figure 40.

LOG EXPOSURE	AMOUNT OF IODIDE TRANSFERRED X 10^{-4} (moles/meter ²)							
	CONTROL	3.98	13.71	68.41				
1) $\bar{2}.39$	DENSITY s	.25 .006	.24 -----	.24 -----	.24 -----	.24 -----	.24 -----	.24 -----
	F-TEST	.121E+3		.324E 0		.324E+0		
2) $\bar{2}.71$	DENSITY s	.28 .006	.24 -----	.24 -----	.24 -----	.24 -----	.24 -----	.24 -----
	F-TEST	.439E+3		.199E+1		.991E 0		
3) $\bar{2}.99$	DENSITY s	.36 .042	.24 -----	.24 -----	.24 -----	.24 -----	.24 -----	.24 -----
	F-TEST	.329E+3		.991E+0		-----		
4) $\bar{1}.27$	DENSITY s	.51 .050	.24 -----	.24 -----	.24 -----	.24 -----	.24 -----	.24 -----
	F-TEST	.713E+3		.107E+2		.245E+1		
5) $\bar{1}.57$	DENSITY s	.76 .050	.25 .006	.24 -----	.24 -----	.24 -----	.24 -----	.25 -----
	F-TEST	.115E+4		.240E+2		.143E+2		
6) $\bar{1}.84$	DENSITY s	1.03 .071	.29 .018	.24 -----	.24 -----	.25 -----	.24 -----	.27 -----
	F-TEST	.934E+3		.278E+2		.148E+2		
7) $\bar{.}15$	DENSITY s	1.37 .108	.36 .041	.24 -----	.24 -----	.27 .015	.24 -----	.30 -----
	F-TEST	.101E+4		.431E+2		.452E+1		
8) $\bar{.}45$	DENSITY s	1.68 .106	.47 .049	.24 -----	.24 -----	.31 .029	.24 -----	.33 -----
	F-TEST	.107E+4		.580E+2		.709E 0		
9) $\bar{.}74$	DENSITY s	1.92 .116	.59 .071	.24 -----	.24 -----	.36 .041	.24 -----	.37 .013
	F-TEST	.935E+3		.626E+2		.244E+ 0		
10) $\bar{1}.04$	DENSITY s	2.09 .125	.72 .080	.24 -----	.24 -----	.43 .067	.24 -----	.40 .017
	F-TEST	.106E+4		.910E+2		.259E+1		
11) $\bar{1}.32$	DENSITY s	2.17 .114	.81 .049	.24 -----	.24 -----	.49 .056	.24 -----	.44 .042

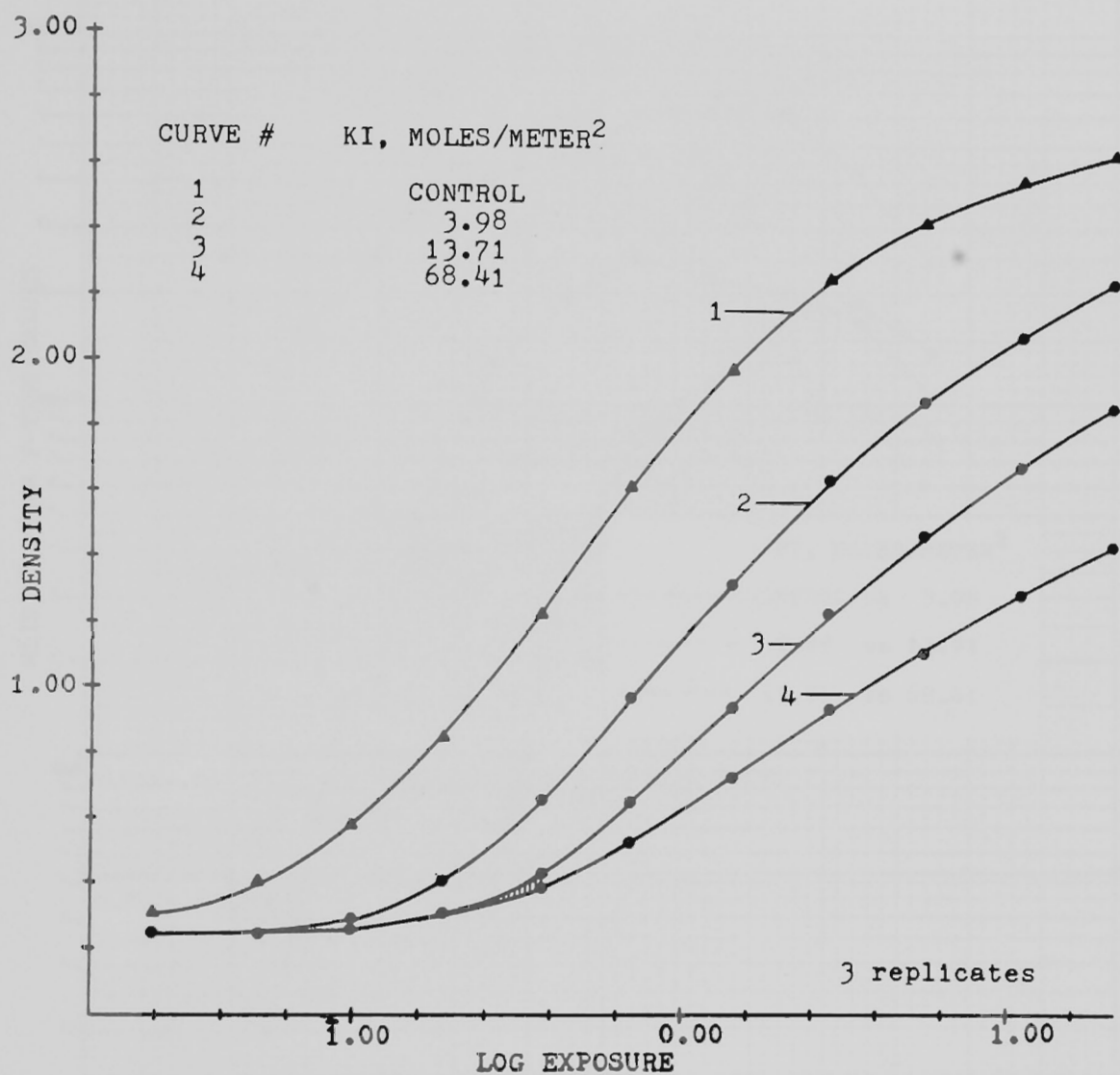


FIGURE 42. Potassium iodide transfer series for Panatomic X film developed in H_2O for ten minutes at 72° Fahrenheit (nitrogen burst agitation).

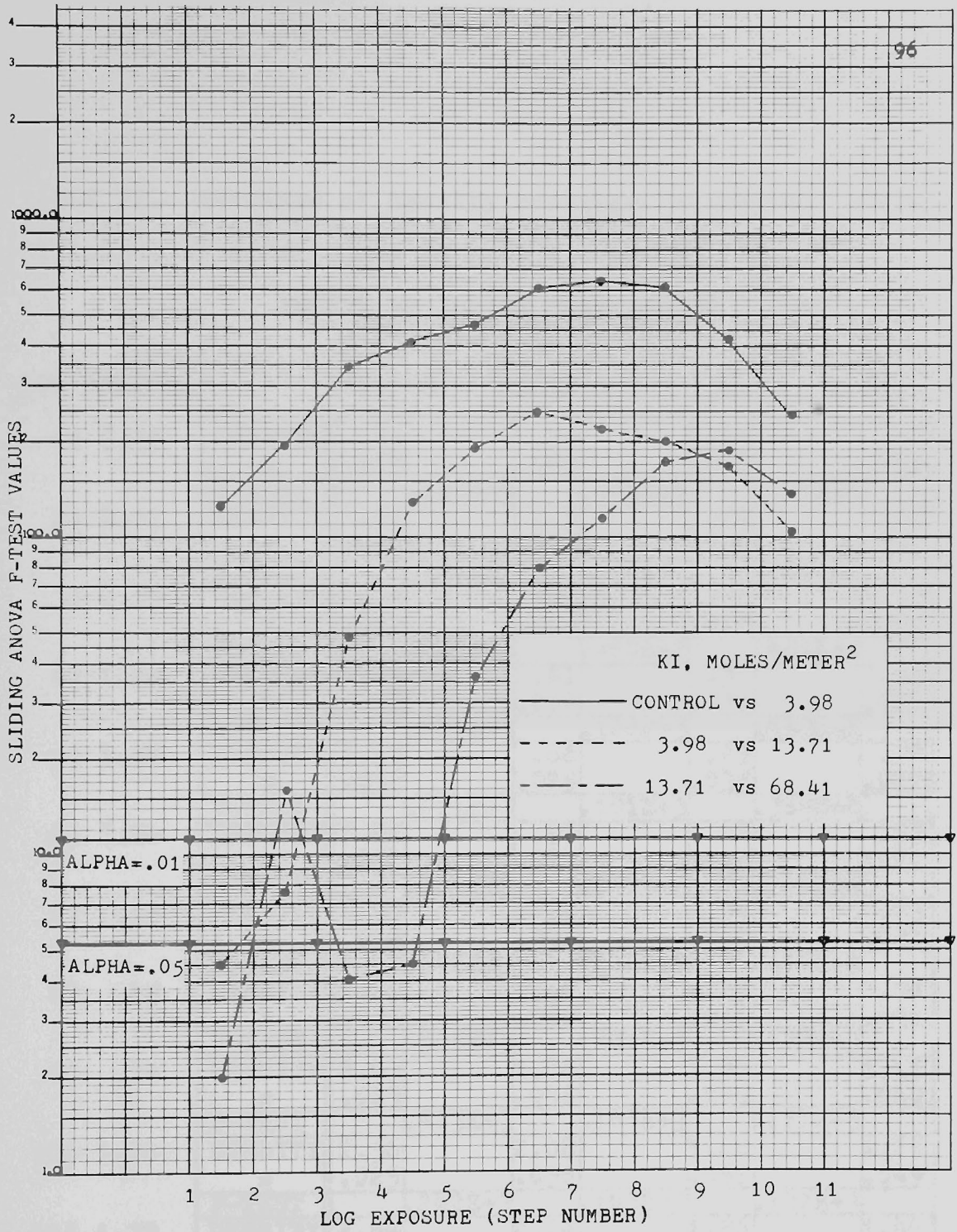


FIGURE 43. Sliding ANOVA F-test values for Figure 42 versus the number of the log exposure step (from Table 22).

TABLE 22. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 42.

AMOUNT OF IODIDE TRANSFERRED X 10^{-4}
(moles/meter²)

LOG EXPOSURE		CONTROL	3.98	13.71	68.41
1) $\bar{2}.39$	DENSITY	.31	.25	.24	.24
	s	.014	.000	.000	.000
	F-TEST	.125E+3	.449E+1	.198E+1	
2) $\bar{2}.71$	DENSITY	.41	.25	.24	.24
	s	.035	.000	.000	.000
	F-TEST	.194E+3	.754E+1	.159E+2	
3) $\bar{2}.99$	DENSITY	.58	.29	.26	.27
	s	.042	.000	.025	.000
	F-TEST	.344E+3	.480E+2	.401E+1	
4) $\bar{1}.27$	DENSITY	.85	.41	.31	.31
	s	.046	.010	.021	.006
	F-TEST	.411E+3	.128E+3	.450E+1	
5) $\bar{1}.57$	DENSITY	1.23	.66	.43	.39
	s	.058	.025	.038	.017
	F-TEST	.471E+3	.191E+3	.364E+2	
6) $\bar{1}.84$	DENSITY	1.62	.97	.65	.53
	s	.052	.029	.044	.021
	F-TEST	.609E+3	.248E+3	.797E+2	
7) .15	DENSITY	1.98	1.32	.94	.73
	s	.047	.042	.040	.031
	F-TEST	.642E+3	.220E+3	.114E+3	
8) .45	DENSITY	2.26	1.64	1.23	.94
	s	.035	.050	.051	.036
	F-TEST	.609E+3	.201E+3	.173E+3	
9) .74	DENSITY	2.43	1.88	1.47	1.11
	s	.023	.046	.049	.040
	F-TEST	.423E+3	.168E+3	.187E+3	
10) 1.04	DENSITY	2.56	2.08	1.68	1.29
	s	.025	.056	.061	.049
	F-TEST	.242E+3	.103E+3	.137E+3	
11) 1.32	DENSITY	2.64	2.24	1.86	1.44
	s	.012	.078	.069	.053

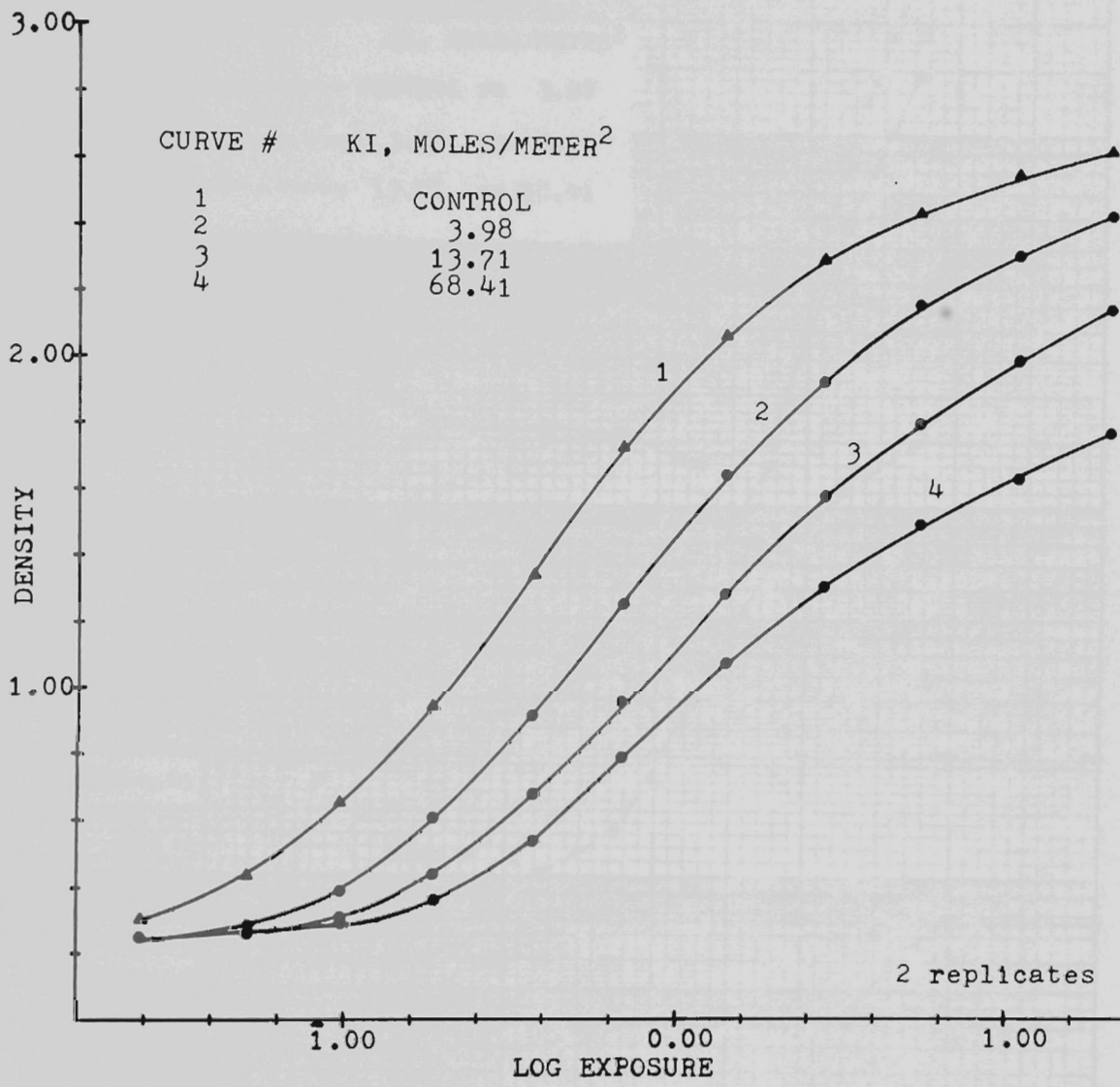


FIGURE 44. Potassium iodide transfer series for Panatomic X film developed in DK-50* for three minutes at 72° Fahrenheit (nitrogen burst agitation).

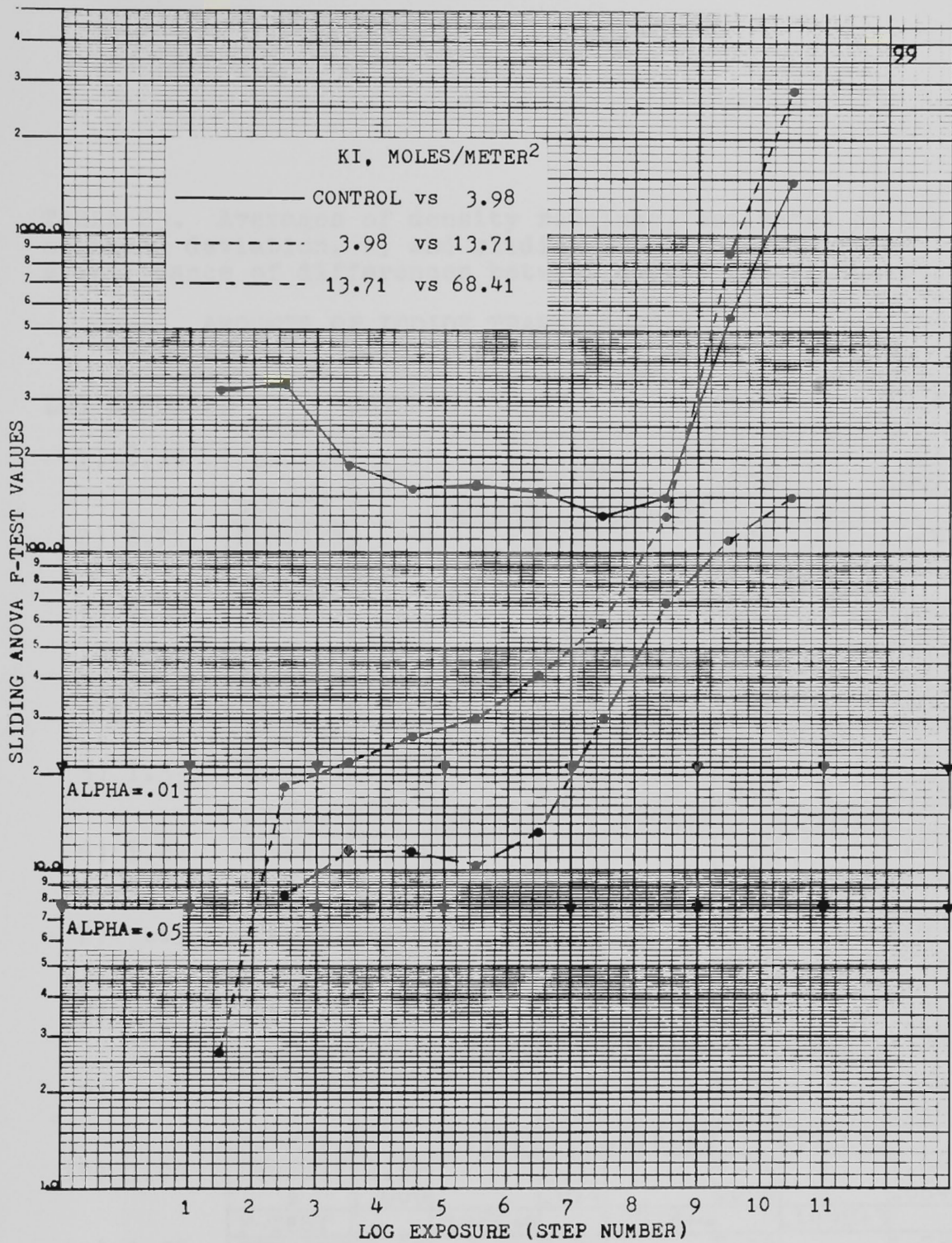


FIGURE 45. Sliding ANOVA F-test values for Figure 44 versus the number of the log exposure step (from Table 23).

TABLE 23. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 44.

AMOUNTS OF IODIDE TRANSFERRED X 10^{-4}
(moles per meter²)

LOG EXPOSURE		CONTROL	3.98	13.71	68.41
1) 2.39	DENSITY	.31	.25	.25	.25
	s	.007	.000	.007	.007
2) 2.71	F-TEST		.322E+3	.266E+1	-----
	DENSITY	.44	.29	.26	.26
3) 2.99	s	.007	.014	.007	.007
	F-TEST		.336E+3	.182E+2	.833E+1
4) 1.27	DENSITY	.66	.39	.31	.29
	s	.007	.028	.007	.007
5) 1.57	F-TEST		.187E+3	.217E+2	.115E+2
	DENSITY	.95	.61	.44	.36
6) 1.84	s	.000	.057	.035	.028
	F-TEST		.157E+3	.261E+2	.114E+2
7) .15	DENSITY	1.35	.92	.68	.54
	s	.014	.064	.064	.057
8) .45	F-TEST		.163E+3	.299E+2	.103E+2
	DENSITY	1.74	1.26	.96	.79
9) .74	s	.028	.071	.078	.071
	F-TEST		.154E+3	.408E+2	.131E+2
10) 1.04	DENSITY	2.08	1.65	1.29	1.08
	s	.007	.071	.071	.071
11) 1.32	F-TEST		.130E+3	.600E+2	.297E+2
	DENSITY	2.31	1.94	1.59	1.31
12) 1.61	s	.007	.071	.042	.064
	F-TEST		.148E+3	.130E+3	.687E+2
13) 1.90	DENSITY	2.45	2.17	1.81	1.50
	s	.007	.028	.014	.064
14) 2.19	F-TEST		.553E+3	.878E+3	.109E+3
	DENSITY	2.57	2.32	2.00	1.64
15) 2.48	s	.000	.014	.000	.064
	F-TEST		.148E+4	.282E+4	.149E+3
16) 2.77	DENSITY	2.64	2.44	2.16	1.78
	s	.007	.007	.000	.057

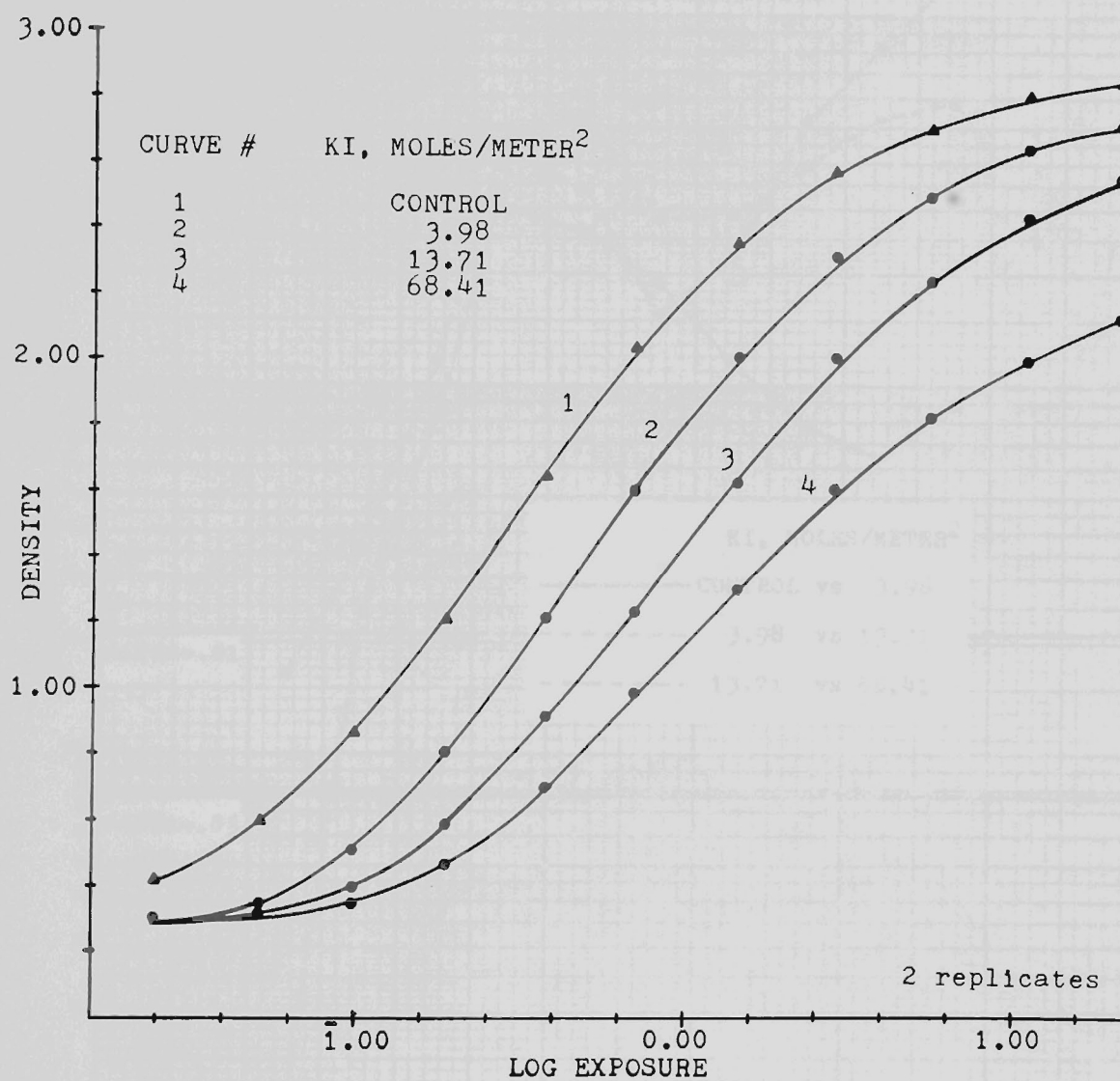


FIGURE 46. Potassium iodide transfer series for Panatomic X film developed in DK-50* for ten minutes at 72° Fahrenheit (nitrogen burst agitation).

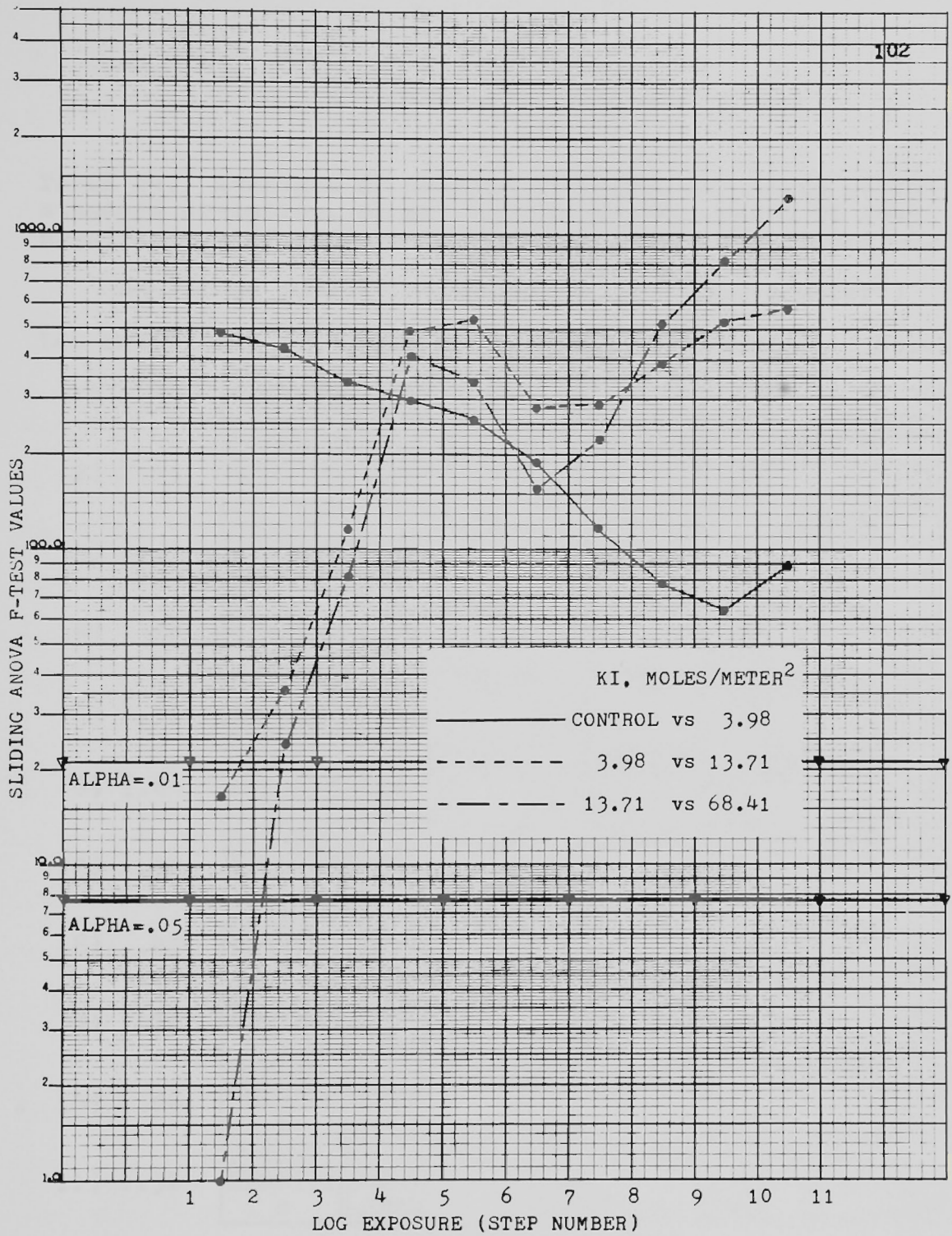


FIGURE 47. Sliding ANOVA F-test values for Figure 46 versus the number of the log exposure step (from Table 24).

TABLE 24. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 46.

		AMOUNT OF IODIDE TRANSFERRED X 10^{-4} (moles/meter ²)				
LOG EXPOSURE		CONTROL	3.98	13.71	68.41	
1) $\bar{2}.39$	DENSITY	.42	.31	.30	.30	
	s	.007	.007	.007	.007	
2) $\bar{2}.71$	F-TEST		.484E+3	.163E+2	.994E 0	
	DENSITY	.60	.35	.32	.31	
3) $\bar{2}.99$	s	.021	.007	.007	.007	
	F-TEST		.432E+3	.356E+2	.240E+2	
4) $\bar{1}.27$	DENSITY	.87	.51	.40	.35	
	s	.021	.028	.014	.007	
5) $\bar{1}.57$	F-TEST		.339E+3	.115E+3	.826E+2	
	DENSITY	1.22	.82	.59	.47	
6) $\bar{1}.84$	s	.042	.014	.014	.007	
	F-TEST		.295E+3	.493E+3	.408E+3	
7) $\bar{.}15$	DENSITY	1.66	1.22	.92	.70	
	s	.050	.014	.000	.007	
8) $\bar{.}45$	F-TEST		.259E+3	.535E+3	.340E+3	
	DENSITY	2.05	1.61	1.24	.99	
9) $\bar{.}74$	s	.057	.014	.035	.000	
	F-TEST		.189E+3	.281E+3	.155E+3	
10) 1.04	DENSITY	2.37	2.02	1.64	1.31	
	s	.057	.000	.050	.028	
11) 1.32	F-TEST		.117E+3	.289E+3	.223E+3	
	DENSITY	2.59	2.33	2.02	1.62	
12) 1.62	s	.057	.000	.028	.028	
	F-TEST		.779E+2	.388E+3	.518E+3	
13) 1.84	DENSITY	2.72	2.51	2.26	1.84	
	s	.049	.007	.028	.028	
14) 2.01	F-TEST		.639E+2	.525E+3	.822E+3	
	DENSITY	2.82	2.66	2.45	2.01	
15) 2.14	s	.042	.000	.000	.028	
	F-TEST		.881E+2	.579E+3	.129E+4	
16) 2.14	DENSITY	2.86	2.73	2.57	2.14	
	s	.000	.007	.021	.000	

obtained. At three and five minutes development time, the transferred iodide had a pronounced retarding effect on development (Figure 38 and Figure 40). For a development time of ten minutes (Figure 42) a more familiar set of characteristic curves was produced. The results with Pan X contrast sharply to the acceleration of development by iodide for Cine Positive developed in the H₂Q developer.

Analysis of the unexpected results with the H₂Q developer must take into consideration the assumed relative complexity of Panatomic X film as compared to Cine Positive 5302 film. During the transfer of iodide to Pan X, it was noticed that the Bimat web transfer medium acquired a yellowish color evidently obtained from the film. It is suspected that there are several unknown constituents incorporated into the emulsion for various purposes. Spectrophotometric evaluation of undeveloped Panatomic X using a Beckman DK 2A Spectrophotometer revealed several absorption peaks in the wavelength region from 450 to 700 nanometers that were not present in the Cine Positive spectrophotometric traces. These peaks are assumed to be the result of sensitizing dyes and other unknown substances in the emulsion. Therefore, considering the problem of not knowing the nature of the constituents which go into the preparation of Panatomic X film, it is not advisable to be too hasty in drawing conclusions from the results obtained with the H₂Q developer and Pan X

film combination. It is quite possible that transferred iodide had such a pronounced retarding effect on Pan X because of an interaction with one of the unknown constituents of Pan X.

To facilitate comparison of Pan X results with the different developers, Figure 48 was prepared showing the density attained for a .45 log exposure for the iodide transfer series at development times of three and ten minutes. Referring to Figure 48, the retardation for DK-50 and DK-50* appears similar to the results obtained for Cine Positive developed in those developers. Development of Pan X with H₂Q developer deviated radically from the results obtained with Cine Positive, although at a development time of ten minutes the densities for Pan X were better behaved.

Figure 49 and Figure 50 show the values of contrast index and the relative speeds for Pan X film developed in DK-50, H₂Q, and DK-50* developers. The results, again, are analagous to those obtained for Cine Positive developed in DK-50 and DK-50*, but the H₂Q results are quite different.

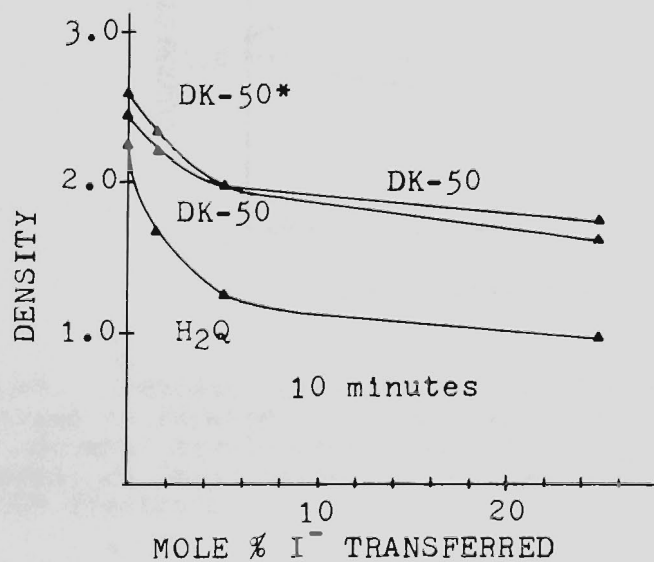
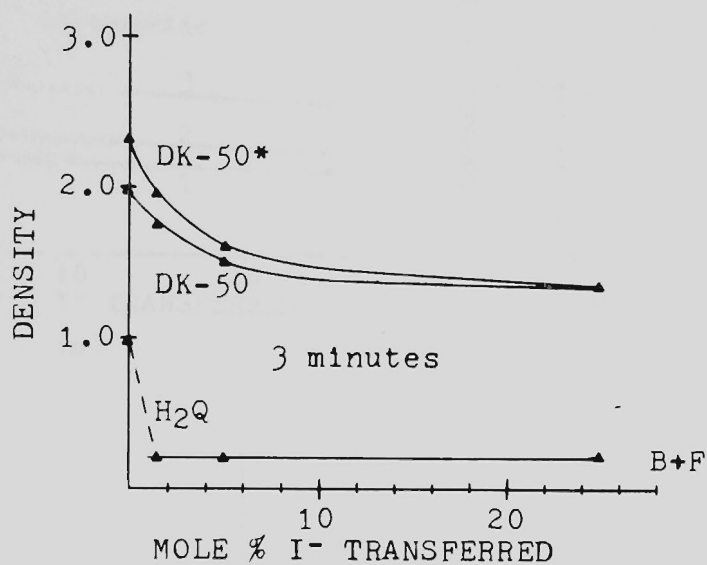
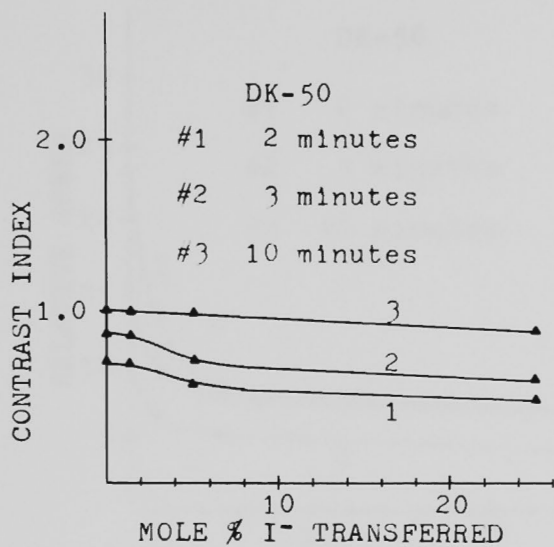
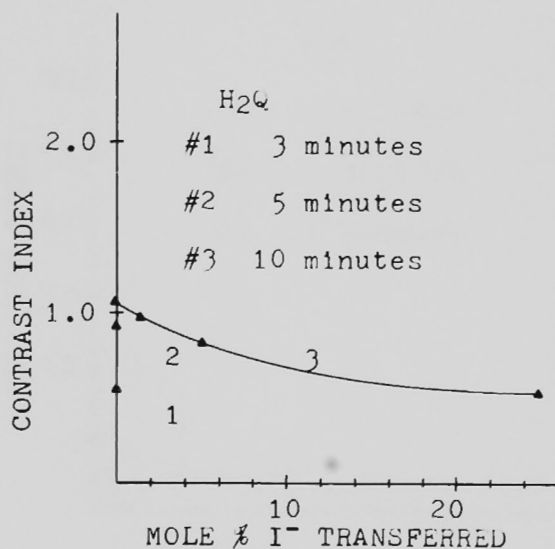


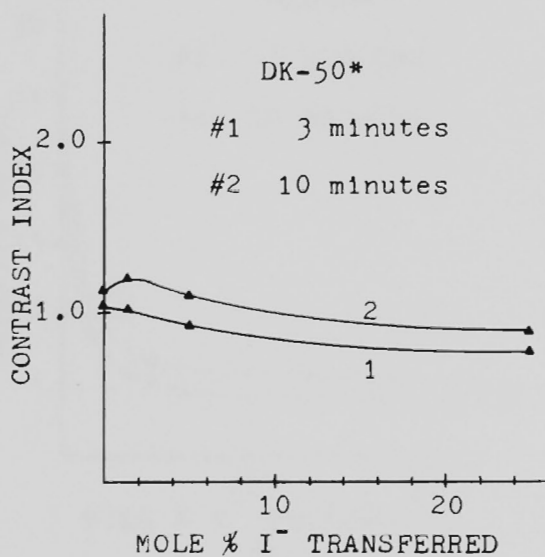
FIGURE 48. Intercomparison of Panatomic X iodide transfer series at one exposure level (log exposure = .45) for development with three developers and two times of development.



(a)



(b)



(c)

FIGURE 49. Contrast index versus the amount of iodide transferred to Panatomic X film (expressed in mole per cent). Several development times are included for three developers; a) DK-50 developer, b) H₂Q developer, and c) DK-50* developer.

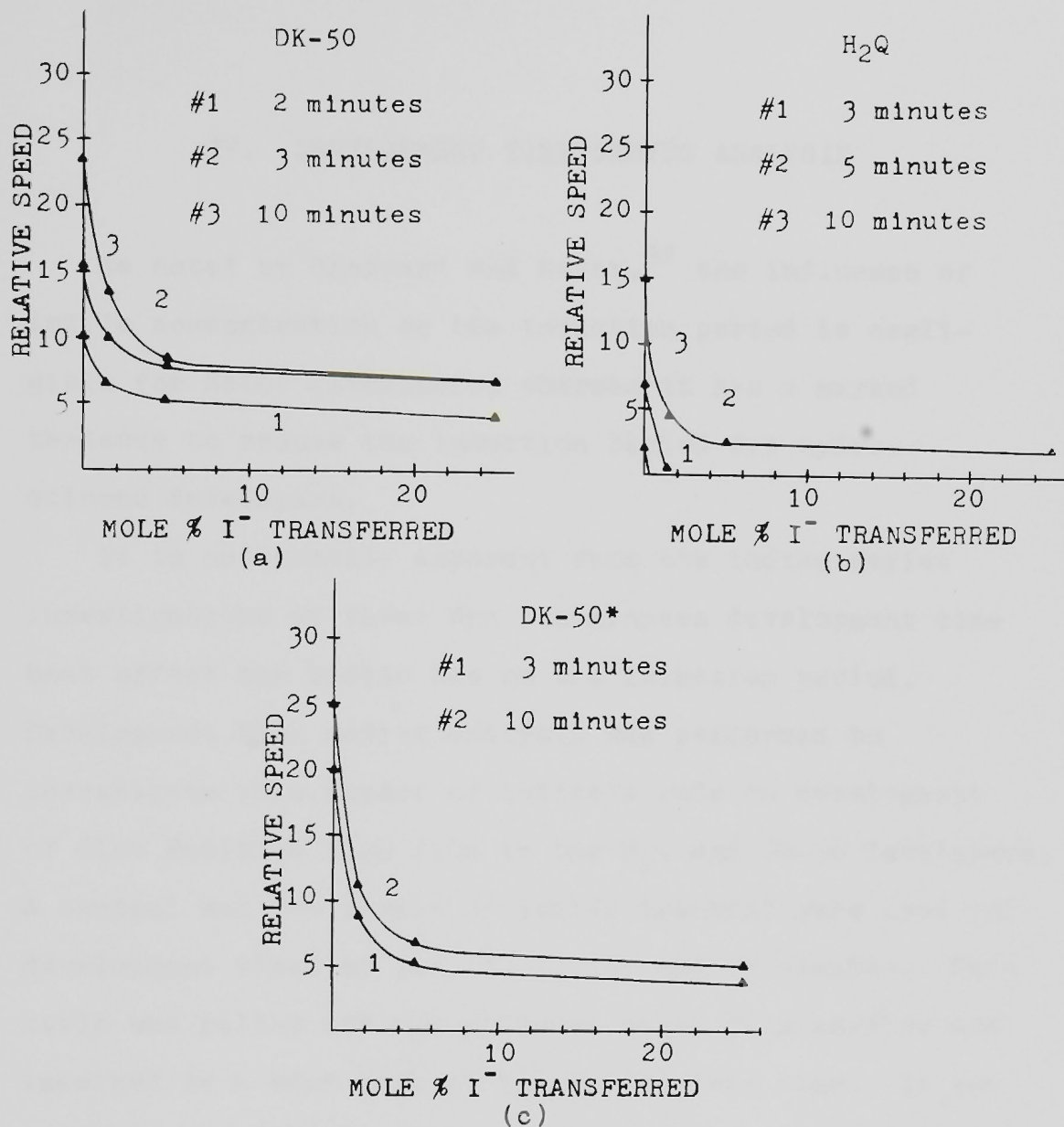


FIGURE 50. Relative speed versus the amount of iodide transferred to Panatomic X film (expressed in mole per cent). Several development times are included for three developers; a) DK-50 developer, b) H₂Q developer, and c) DK-50* developer.

IV. DEVELOPMENT TIME SERIES ANALYSIS

As noted by Sheppard and Meyer,³² the influence of iodide concentration on the induction period is negligible for Metol developers, whereas it has a marked tendency to reduce the induction period for hydroquinone developers.

It is not readily apparent from the iodide series investigations at three and ten minutes development time what effect the iodide has on the induction period. Development time series analysis was performed to investigate this aspect of iodide's role in development of Cine Positive 5302 film in the H₂Q and DK-50 developers. A control and two levels of iodide transfer were used for development times of 1.5, 3, 5, 10, and 15 minutes. Each strip was pulled off the nitrogen burst film carrier and immersed in a stop bath at the appropriate time. It was expected that the procedure of raising the film carrier out of the nitrogen burst tank to remove test strips at different times would provide another source of variability due to the noncontinuity of agitation, but effort was made to minimize the time the film carrier was out of the developing solution. The results of these investigations

for DK-50 and H₂Q are found in Figure 51 and Figure 52, respectively. The values for these graphs are found in Table 25 and Table 26. Sliding ANOVA F-tests were also tabulated in Table 25 and Table 26. Figure 53 and Figure 54 are composites of the data for each developer at four selected exposure levels to enable intercomparison of the iodide transfer data and the control data. As is readily apparent from the data for low development times, H₂Q developer has a marked induction period, whereas the DK-50 developer has a much smaller one. It is also quite apparent that iodide tends to reduce the induction period of the H₂Q developer for both levels of iodide transfer which were tested, but as expected, there is no indication that iodide reduces the induction period for DK-50 developer. Various proposed schemes of representing the induction period have been proposed in the photographic literature. In the absence of a standard and because a precise definition is not needed here, a simple evaluation of the densities obtained at low development times is used to describe relative induction periods. The composite data demonstrates the relative effects of transferred iodide at two levels and the control with no iodide transferred. For DK-50 development (Figure 53), it is apparent that no acceleration occurs for either concentration of transferred iodide. The low concentrations of iodide retarded development more at longer development

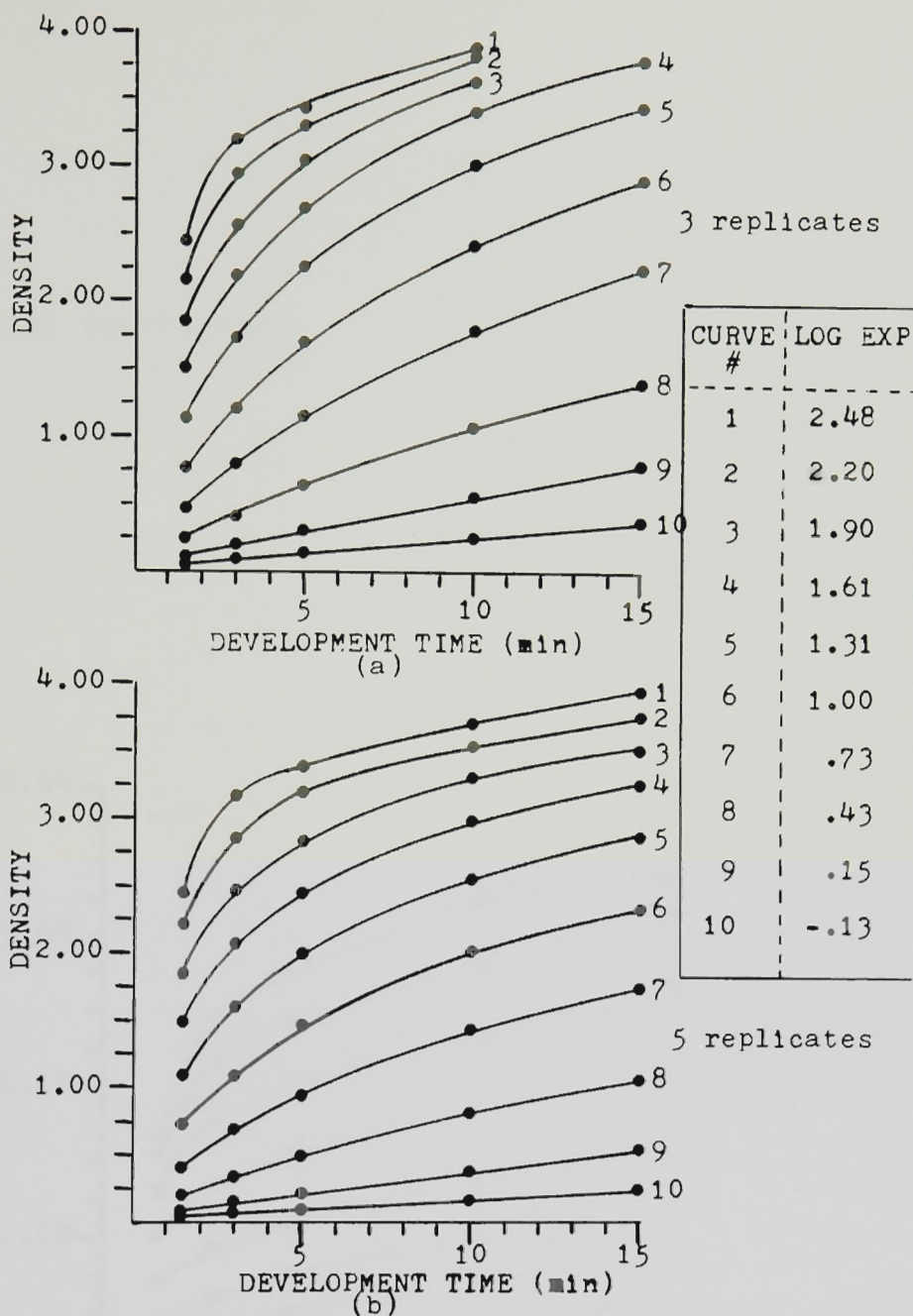
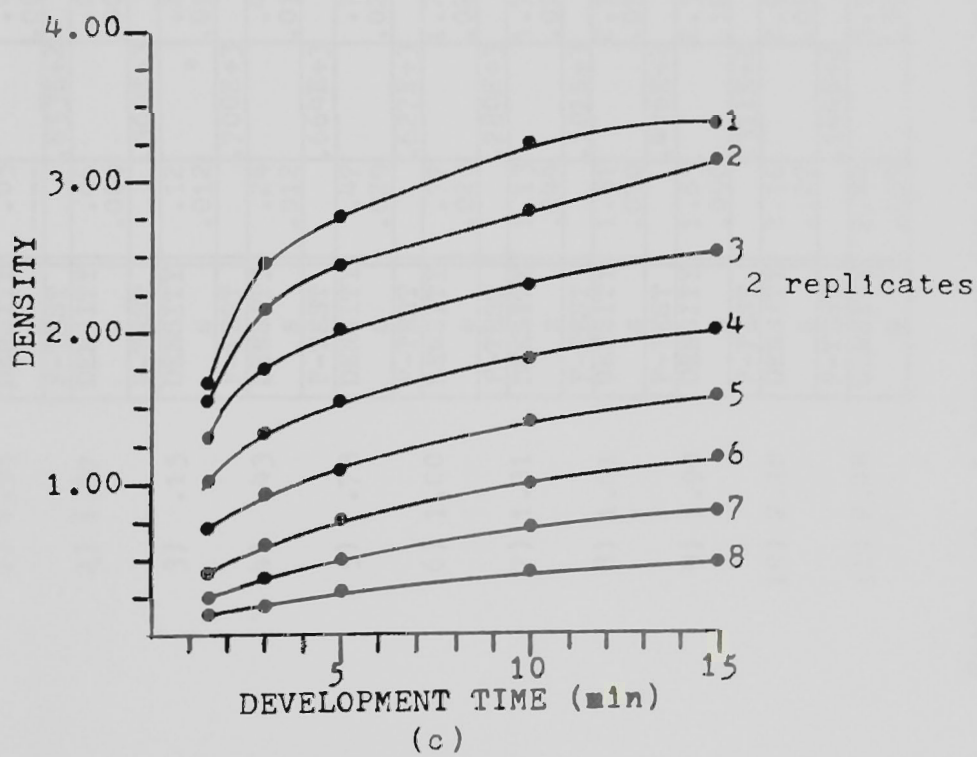


FIGURE 51. Development time series for Cine Positive film developed in DK-50 at 72° Fahrenheit using nitrogen burst agitation; a) Control-no iodide transferred, b) 3.98×10^{-4} moles of KI per square meter was transferred, and c) 68.41×10^{-4} moles of KI per square meter was transferred.

FIGURE 51 (continued)



LOG EXPOSURE	DEVELOPMENT TIME, MINUTES										
	1.5	3.0	5.0	10.0	15.0	15.0	10.0	5.0	3.0	1.5	
1) 1.55	DENSITY s	.05	.06 .006	.07 .006	.13 .006	.21 .015					
	F-TEST	---	.853E+2	.320E+3	.152E+4	.803E+3					
2) 1.87	DENSITY s	.06 .000	.09 .006	.14 .000	.25 .000	.37 .006					
	F-TEST	.300E+3	.131E+4	.972E+4	.412E+4						
3) .15	DENSITY s	.12 .012	.20 .010	.30 .006	.55 .006	.78 .017					
	F-TEST	.700E+3	.105E+4	.220E+4	.238E+4						
4) .43	DENSITY s	.24 .012	.41 .010	.64 .025	1.07 .017	1.41 .032					
	F-TEST	.664E+3	.102E+4	.195E+4	.271E+4						
5) .73	DENSITY s	.47 .029	.79 .025	1.16 .032	1.79 .020	2.23 .030					
	F-TEST	.627E+3	.492E+3	.630E+3	.136E+4						
6) 1.00	DENSITY s	.77 .020	1.21 .025	1.70 .058	2.42 .042	2.90 .027					
	F-TEST	.280E+3	.261E+3	.397E+3	.101E+4						
7) 1.31	DENSITY s	1.13 .044	1.73 .072	2.27 .064	3.02 .032	3.44 .021					
	F-TEST	.101E+3	.937E+2	.161E+3	.406E+3						
8) 1.61	DENSITY s	1.51 .070	2.19 .095	2.69 .081	3.41 .023	3.78 .044					
	F-TEST	.476E+2	.514E+2	.789E+2	.196E+3						
9) 1.90	DENSITY s	1.85 .090	2.57 .107	3.04 .070	3.63 .023	---					
	F-TEST	.311E+2	.414E+2	.590E+2	.617E+2						
10) 2.20	DENSITY s	2.16 .127	2.94 .092	3.30 .060	3.82 .035	---					
	F-TEST	.144E+2	.191E+2	.158E+2	.116E+2						
11) 2.48	DENSITY s	2.44 .159	3.19 .085	3.43 .049	3.89 .006	---					

TABLE 25a. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 51a.

DEVELOPMENT TIME, MINUTES

LOG EXPOSURE	1.5	3.0	5.0	10.0	15.0
1) 1.55	DENSITY s .05 .006	.05 .005	.06 .006	.10 .071	.15 .009
2) 1.87	F-TEST DENSITY s .06 .006	.893E+2 .08 .008	.427E+3 .10 .005	.254E+3 .17 .005	.24 .015
3) 1.15	F-TEST DENSITY s .10 .007	.415E+3 .16 .008	.844E+3 .22 .011	.788E+3 .38 .015	.54 .025
4) 1.43	F-TEST DENSITY s .21 .007	.107E+4 .34 .013	.120E+4 .49 .016	.111E+4 .82 .026	.111E+4 1.06 .034
5) 1.73	F-TEST DENSITY s .42 .011	.127E+4 .69 .028	.110E+4 .94 .033	.914E+3 1.43 .045	.105E+4 1.73 .034
6) 1.00	F-TEST DENSITY s .73 .013	.880E+3 1.09 .041	.805E+3 1.47 .037	.445E+3 2.01 .068	.373E+3 2.32 .058
7) 1.31	F-TEST DENSITY s 1.10 .015	.100E+4 1.60 .039	.809E+3 2.00 .039	.290E+3 2.54 .074	.225E+3 2.85 .047
8) 1.61	F-TEST DENSITY s 1.49 .021	.101E+4 2.07 .044	.745E+3 2.44 .026	.176E+3 2.98 .078	.127E+3 2.25 .058
9) 1.90	F-TEST DENSITY s 1.86 .035	.949E+3 2.47 .039	.821E+3 2.83 .037	.156E+3 3.30 .052	.740E+2 3.51 .050
10) 2.20	F-TEST DENSITY s 2.21 .050	.318E+3 2.86 .058	.338E+3 3.19 .038	.218E+3 3.53 .018	.927E+2 3.74 .045
11) 2.48	F-TEST DENSITY s 2.44 .098	.754E+2 3.17 .030	.154E+3 3.39 .050	.893E+2 3.70 .067	.679E+2 3.93 .061

TABLE 25b. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 51b.

DEVELOPMENT TIME, MINUTES

LOG EXPOSURE	DEVELOPMENT TIME, MINUTES										
	1.5	3.0	5.0	10.0	15.0						
1) 1.55	DENSITY s	.04 .007	.05 .007	.07 .007	.10 .028	.11 .007					
2) 1.87	F-TEST DENSITY s	.05 .000	.07 .000	.09 .007	.13 .035	.15 .000	.163E+2	.281E+1	.467E+1		
3) .15	F-TEST DENSITY s	.07 .007	.10 .007	.15 .007	.23 .042	.26 .007	.120E+3	.153E+2	.285E+2		
4) .43	F-TEST DENSITY s	.13 .014	.20 .007	.28 .014	.41 .050	.47 .021	.289E+3	.427E+2	.657E+2		
5) .73	F-TEST DENSITY s	.24 .028	.37 .014	.49 .021	.70 .064	.80 .035	.321E+3	.713E+2	.938E+2		
6) 1.00	F-TEST DENSITY s	.40 .028	.59 .007	.75 .021	.99 .007	1.16 .021	.354E+3	.121E+3	.146E+3		
7) 1.31	F-TEST DENSITY s	.70 .007	.93 .000	1.08 .007	1.40 .007	1.57 .007	.792E+3	.182E+4	.223E+4		
8) 1.61	F-TEST DENSITY s	1.02 .021	1.33 .000	1.53 .000	1.82 .014	2.01 .028	.207E+4	.510E+4	.132E+4		
9) 1.90	F-TEST DENSITY s	1.30 .007	1.75 .007	2.01 .014	2.31 .007	2.53 .021	.179E+4	.445E+4	.141E+4		
10) 2.20	F-TEST DENSITY s	1.54 .042	2.15 .021	2.44 .021	2.81 .021	3.14 .149	.343E+3	.153E+4	.107E+3		
11) 2.48	F-TEST DENSITY s	1.67 .106	2.46 .021	2.77 .070	3.26 .021	3.38 .021	.284E+2	.189E+3	.408E+2		

TABLE 25c. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 51c.

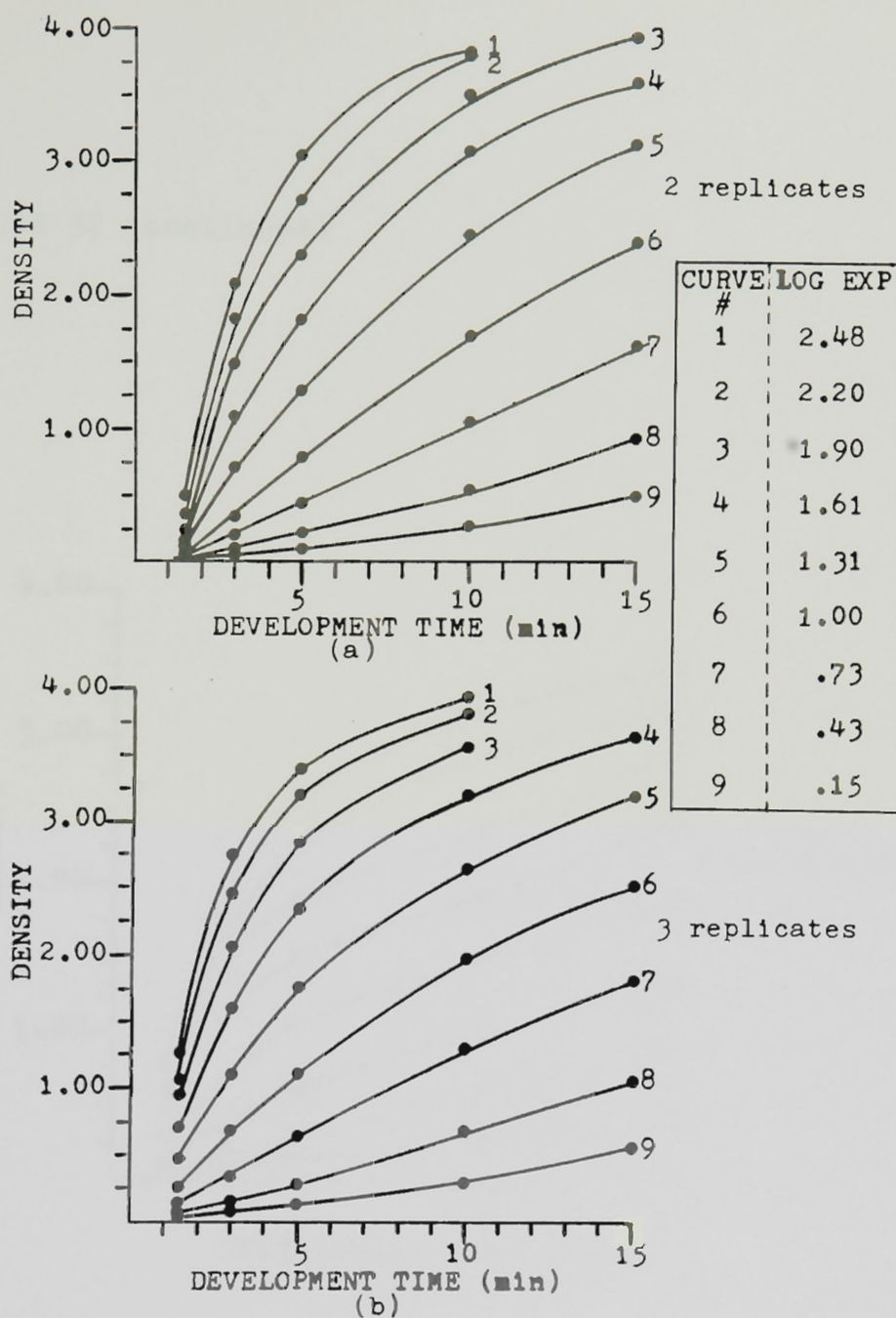
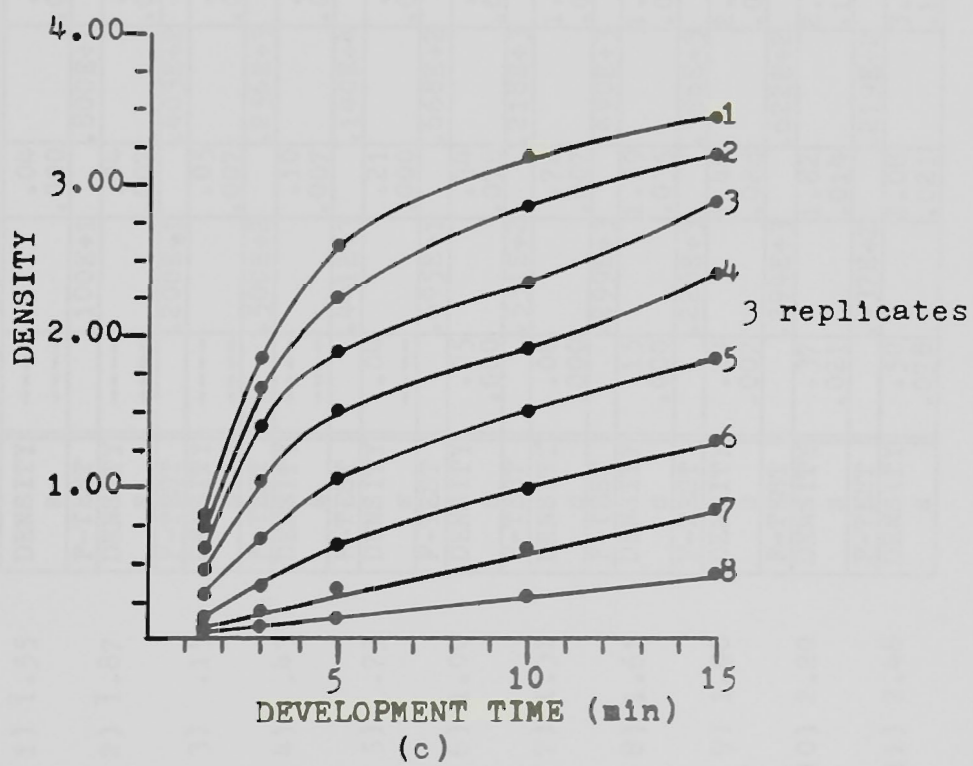


FIGURE 52. Development time series for Cine Positive film developed in H_2O at 72° Fahrenheit using nitrogen burst agitation; a) Control-no iodide transferred, b) 3.98×10^{-4} moles of iodide transferred per square meter, c) 68.41×10^{-4} moles of iodide transferred per square meter.

FIGURE 52 (continued)



DEVELOPMENT TIME, MINUTES

LOG EXPOSURE	1.5	3.0	5.0	10.0	15.0
1) 1.55	DENSITY s ---- ---- ---- ----	.04 .000	.05 .007	.09 .014	.19 .028
2) 1.87	F-TEST DENSITY s ---- ---- ---- ----	.100E+1 .04 .007	.800E+1 .07 .000	.327E+2 .14 .007	.261E+2 .27 .021
3) .15	F-TEST DENSITY s ---- ---- ---- ----	.200E+1 .05 .007	.403E+2 .11 .007	.409E+3 .27 .007	.245E+3 .49 .021
4) .43	F-TEST DENSITY s ---- ---- ---- ----	.500E+2 .10 .007	.256E+3 .22 .007	.144E+4 .54 .007	.981E+3 .92 .021
5) .73	F-TEST DENSITY s .04 ---- ---- ----	.441E+3 .21 .000	.140E+4 .44 .007	.302E+4 1.05 .014	.749E+3 1.63 .057
6) 1.00	F-TEST DENSITY s .05 .000 ---- ----	.695E+1 .34 .078	.668E+2 .79 .028	.182E+4 1.70 .007	.118E+4 2.40 .007
7) 1.31	F-TEST DENSITY s .08 .000 ---- ----	.551E+2 .72 .007	.218E+3 1.29 .014	.288E+4 2.45 .007	.856E+4 3.14 .021
8) 1.61	F-TEST DENSITY s .15 .000 ---- ----	.299E+3 1.09 .035	.490E+3 1.82 .042	.940E+3 3.08 .028	.947E+3 3.61 .036
9) 1.90	F-TEST DENSITY s .24 .007 ---- ----	.220E+3 1.48 .028	.196E+3 2.31 .064	.240E+3 3.50 .021	.419E+3 3.94 .014
10) 2.20	F-TEST DENSITY s .37 .021 ---- ----	.294E+3 1.82 .014	.622E+2 2.72 .113	.560E+2 3.80 .014	.306E+3 ---- ----
11) 2.48	F-TEST DENSITY s .50 .078 ---- ----	.437E+2 2.08 .021	.219E+2 3.06 .141	.746E+1 3.82 .042	.224E+0 ---- ----

TABLE 26a. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 52a.

DEVELOPMENT TIME, MINUTES

LOG EXPOSURE	1.5	3.0	5.0	10.0	15.0
1) 1.55	DENSITY s .04 .000	.05 .006	.06 .006	.11 .010	.21 .040
2) 1.87	F-TEST s .04 .000	.160E+1 .06 .006	.160E+2 .07 .006	.490E+2 .16 .012	.199E+2 .30 .035
3) 1.15	F-TEST s .05 .000	.999E+2 .08 .000	.208E+3 .13 .006	.305E+3 .31 .015	.143E+3 .56 .045
4) 1.43	F-TEST s .07 .000	.300E+3 .16 .010	.280E+3 .28 .021	.573E+3 .68 .027	.326E+3 1.06 .062
5) 1.73	F-TEST s .14 .010	.250E+3 .35 .025	.383E+3 .63 .035	.114E+4 1.30 .012	.898E+3 1.82 .040
6) 1.00	F-TEST s .26 .015	.264E+3 .68 .035	.306E+3 1.12 .057	.814E+3 1.98 .020	.171E+4 2.52 .035
7) 1.31	F-TEST s .47 .035	.254E+3 1.11 .047	.260E+3 1.76 .081	.442E+3 2.65 .038	.150E+4 3.21 .027
8) 1.61	F-TEST s .71 .061	.173E+3 1.60 .046	.212E+3 2.35 .076	.239E+3 3.21 .055	.262E+3 3.65 .079
9) 1.90	F-TEST s .95 .084	.102E+3 2.06 .038	.211E+3 2.84 .059	.153E+3 3.57 .040	.108E+3 ----- -----
10) 2.20	F-TEST s 1.07 .099	.491E+2 2.45 .056	.125E+3 3.21 .076	.140E+3 3.82 .021	.352E+2 ----- -----
11) 2.48	F-TEST s 1.27 .111	.236E+2 2.74 .031	.456E+2 3.40 .072	.260E+2 3.94 .051	.106E+2 ----- -----

TABLE 26b. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 52b.

DEVELOPMENT TIME, MINUTES

LOG EXPOSURE	DEVELOPMENT TIME, MINUTES										
	1.5	3.0	5.0	10.0	15.0						
1) 1.55	DENSITY s	----	----	.04 .000	.06 .006	.08 .006					
2) 1.87	F-TEST s	----	.04 .000	.05 .006	.08 .006	.11 .021					
3) .15	F-TEST s	----	.05 .006	.07 .000	.13 .006	.20 .006					
4) .43	F-TEST s	.04 .006	.08 .012	.14 .006	.28 .012	.43 .030					
5) .73	F-TEST s	.07 .000	.18 .010	.33 .035	.60 .038	.85 .072					
6) 1.00	F-TEST s	.14 .010	.35 .021	.63 .064	.99 .045	1.31 .107					
7) 1.31	F-TEST s	.29 .031	.67 .049	1.06 .081	1.51 .066	1.86 .079					
8) 1.61	F-TEST s	.46 .040	1.03 .012	1.51 .058	1.92 .108	2.42 .078					
9) 1.90	F-TEST s	.60 .045	1.40 .042	1.91 .015	2.36 .096	2.89 .044					
10) 2.20	F-TEST s	.74 .060	1.66 .066	2.66 .090	3.87 .086	5.21 .170					
11) 2.48	F-TEST s	.82 .059	1.85 .085	2.61 .105	3.20 .052	3.46 .114					

TABLE 26c. Averages of density readings, estimates of the standard deviation, s, and sliding ANOVA F-tests of the significance of differences between curves for Figure 52c.

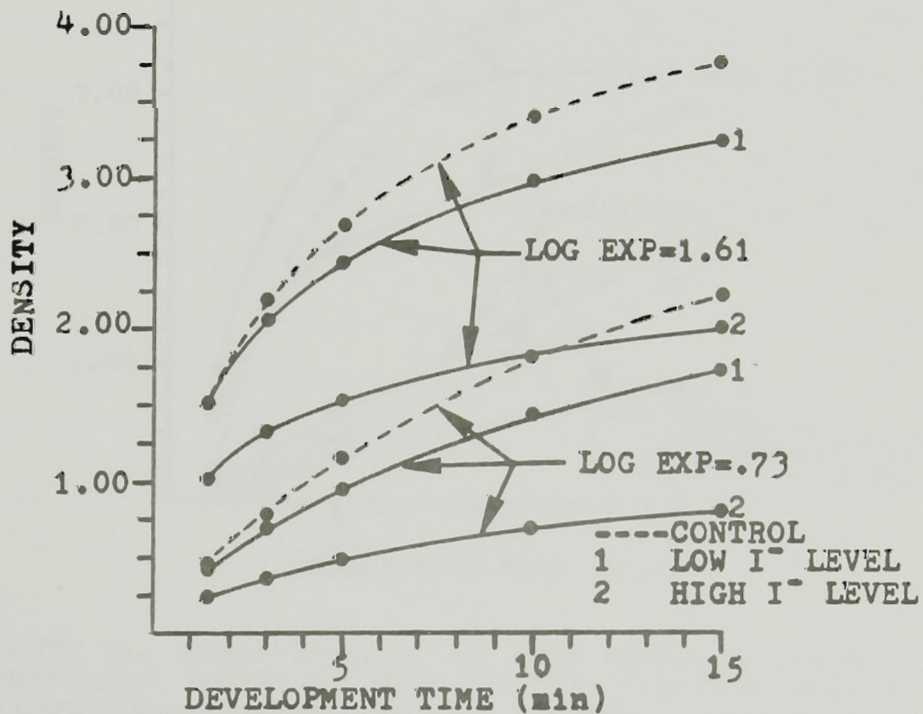
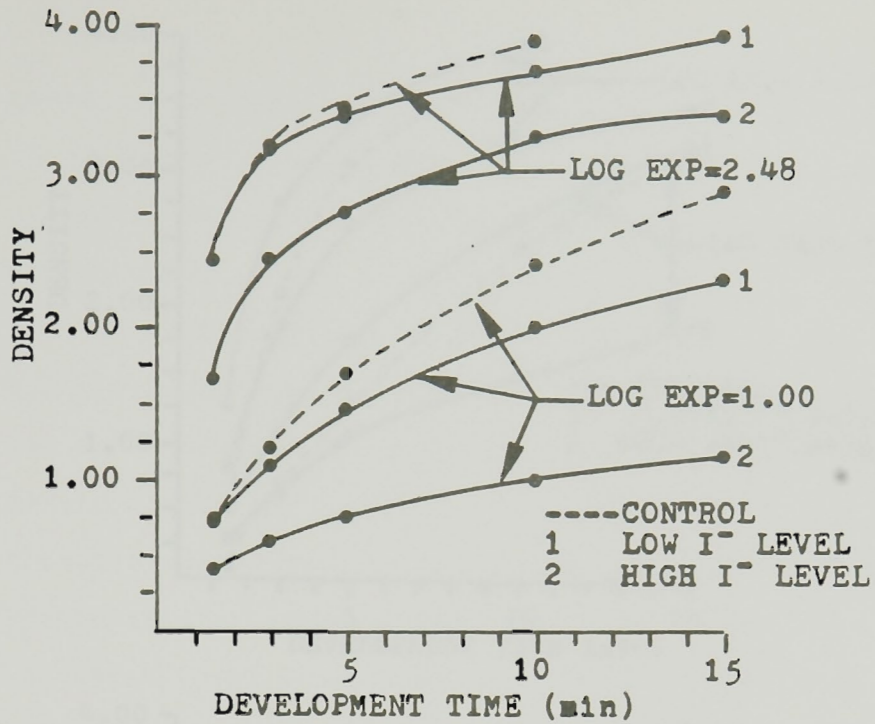


FIGURE 53. Comparisons of Br⁻ only versus two amounts of transferred iodide for Cine Positive film developed in DK-50. The data was first plotted in Figure 51 on separate graphs.

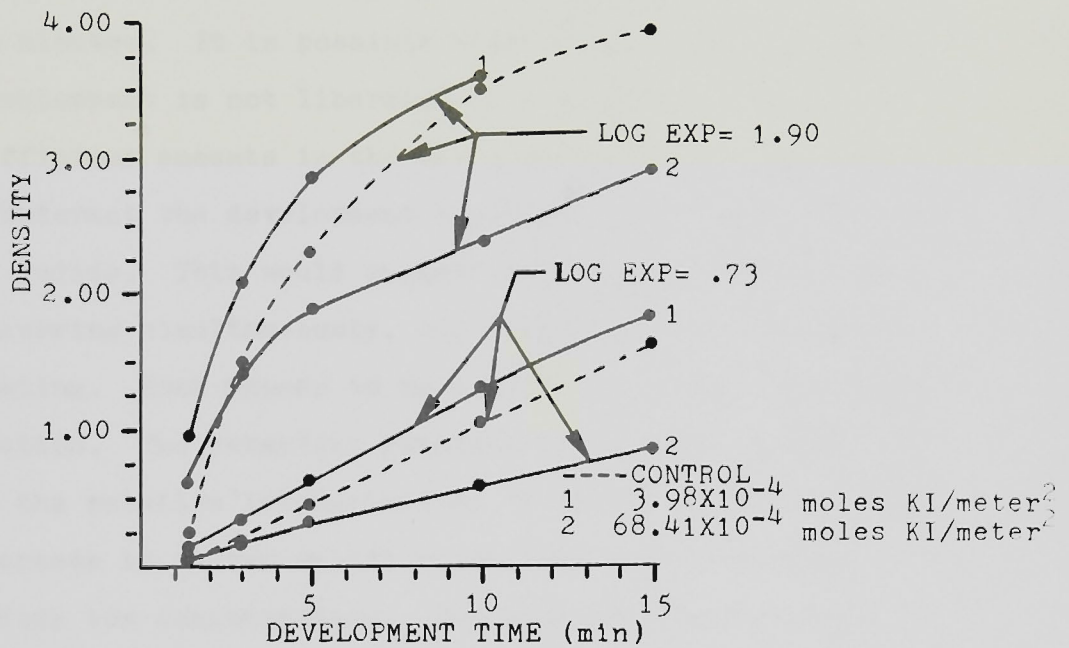
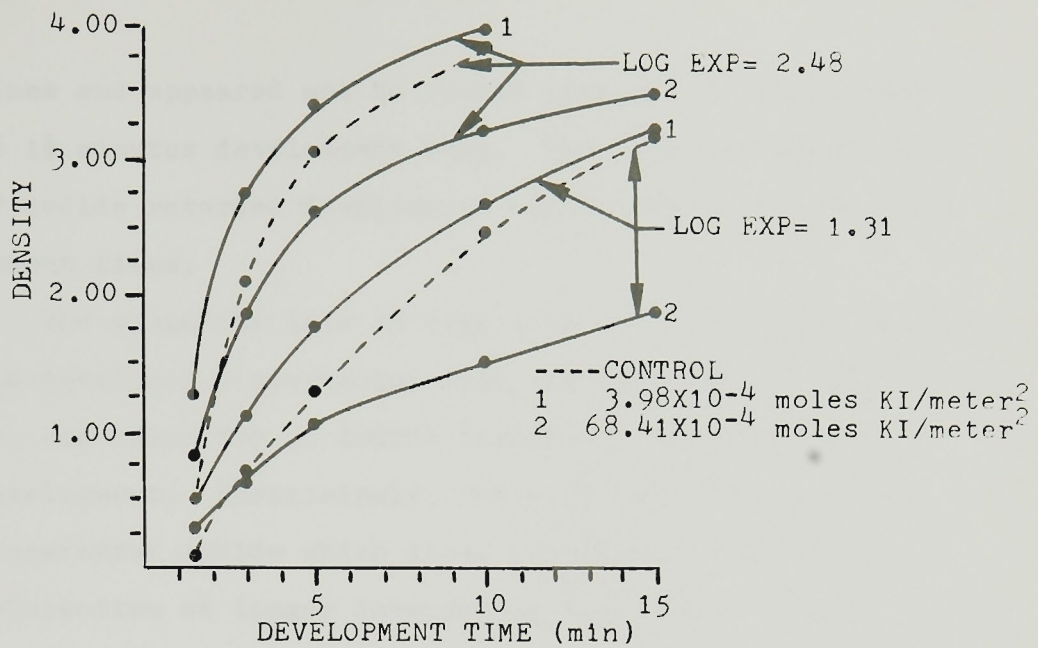


FIGURE 54. Comparisons of Br^- only versus two amounts of transferred iodide for Cine Positive film developed in a hydroquinone developer (H_2Q). The values were first plotted in Figure 52 on separate graphs.

times and appeared not to retard development significantly at $1\frac{1}{2}$ minutes development time. The high concentration of iodide retarded development significantly at all development times.

The composite data in Figure 54 for development by the H₂Q developer demonstrated that the acceleration by the low concentration of iodide disappears with prolonged development. Surprisingly, the high concentration of transferred iodide which gives pronounced development retardation at longer development times gave a small acceleration of development for a development time of $1\frac{1}{2}$ minutes. It is possible that iodide liberated during development is not liberated at a sufficient rate or in sufficient amounts in the early stages of development to counteract the development acceleration of small amounts of iodide. This would suggest that two reactions are occurring simultaneously, one retarding and one accelerating. Both appear to be a function of iodide concentration. The retarding reaction is at least in part due to the relative irreducibility of silver iodide and the decrease in silver halide solubility with increasing iodide ion concentration. The accelerating reaction, which is known as the Lainer Effect, perhaps involves iodide catalyzed enhancement of developer adsorption to the silver halide grain.³³

Both the H₂Q and DK-50 sets of data for the high concentration of iodide transfer show development retardation which does not tend to disappear with prolonged development. This is of particular significance as a possible explanation for edge effects which do not disappear with prolonged development times.³⁴ If the iodide released across a developing edge causes retardation which contributes to the creation of edge effects, then the permanency of the retardation would tend to perpetuate the edge effects even at long development times.

V. SUMMARY

The experiments involving transfer of iodide to Cine Positive and Panatomic X films for three different developers indicated that iodide released during development plays a complex role in the development process. Development acceleration of hydroquinone by iodide (Lainer Effect) was observed for Cine Positive film developed in the H_2Q developer for three minutes (the acceleration disappeared for a development time of ten minutes). Pronounced retardation by iodide occurred for Panatomic X film also developed in H_2Q . The reason for the latter results are not known.

As shown in Figure 53, the iodide induced retardation of Cine Positive film developed in DK-50 indicated that the retardation does not tend to disappear with prolonged development.

The Cine Positive iodide transfer time series investigations in Figure 51 and Figure 52 indicate that iodide reduces the induction period for the H_2Q developer, while it had no apparent effect on the induction period of DK-50 developer. This could account for the development acceleration by iodide noted for Cine Positive developed

in the H₂Q developer.

The procedure of transferring iodide to an existing emulsion is a nonstandard procedure which results in a product which is not representative of photographic emulsions in general. It is of importance to make this distinction. By converting silver bromide to silver iodide, a different distribution of iodide occurs than would be the case for mixed iodobromide grains with the same halide ratios. Iodide distribution does make a difference in the kinetics of development of iodobromide grains.

Conversion to iodide (in normal processing without transferred iodide) occurs at a rate which depends upon the rate of development and can be expected to produce permanent retardation. By transferring the iodide before development begins, a pure silver iodide phase is formed in the grain. The observed retardation due to iodide transfer is not necessarily similar in nature or in magnitude to iodide released during development. Therefore, it is essential to be cautious when drawing conclusions from the iodide transfer series data. The data definitely contributes to an understanding of the role of iodide released during development when it is considered in its proper perspective.

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APPENDIX A

SLIDING ANOVA

"Sliding ANOVA" is simply an application of Analysis of Variance (ANOVA) accomplished in a stepwise manner which enables determination of the regions between two curves where there is or is not a statistical difference due to curves. It is characterized by segmental ANOVA throughout the range of exposure values where experimental error is suspected to vary with density. Figure A1 illustrates a representative case.

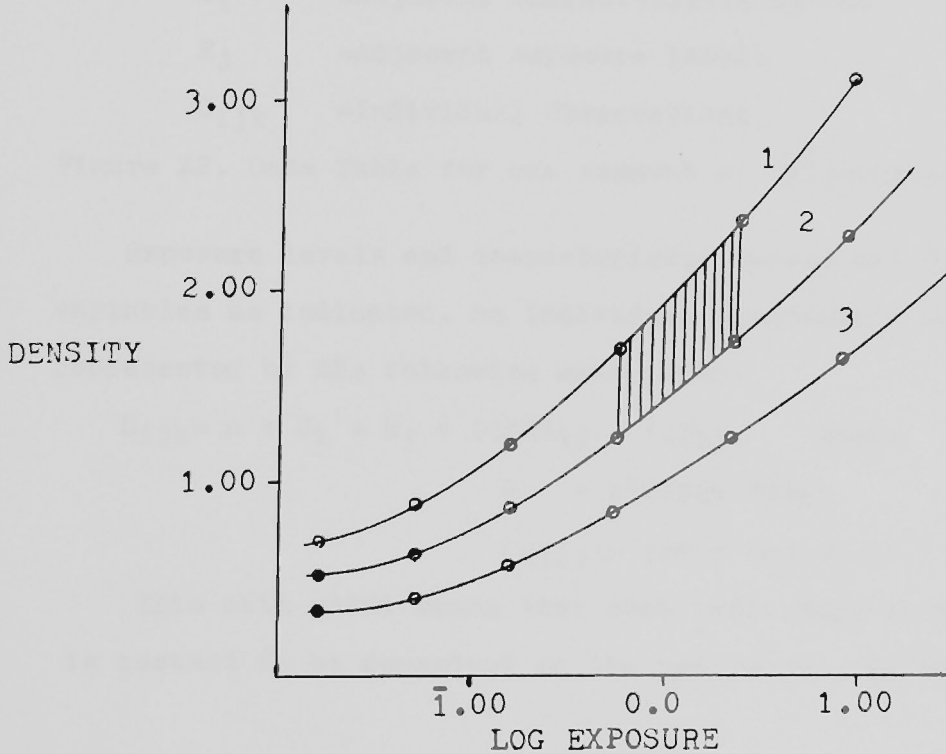


Figure A1. A hypothetical set of characteristic curves.

The blackened area between curve 1 and curve 2 in Figure A1 is just one of fifteen segmental regions for which ANOVA is accomplished using "sliding ANOVA". The data representing this region can be consolidated as in Figure 2.

		FIXED	
		E ₁	E ₂
FIXED	C ₁	D _{1,1,1} D _{1,1,2} D _{1,1,k}	D _{1,2,1} D _{1,2,2} D _{1,2,k}
	C ₂	D _{2,1,1} D _{2,1,2} D _{2,1,k}	D _{2,2,1} D _{2,2,2} D _{2,2,k}

C₁ =Adjacent characteristic curves

E_j =Adjacent exposure levels

D_{ijk} =Individual Observations

Figure A2. Data Table for one segment of "sliding ANOVA".

Exposure levels and characteristic curves are fixed variables as indicated. An individual observation can be represented by the following math model:

$$D_{ijk} = \mu + C_1 + E_j + (CXE)_{1j} + \epsilon_k(1j) \quad \text{where}$$

μ = average value

$\epsilon_k(1j)$ = error nested in i and j

This math model means that each individual observation is assumed to be dependent on the mean value, influences

due to curves, exposures and the interaction between curves and exposures and, also, an error factor. Analysis of Variance is a means for testing such a math model. An ANOVA table as in Figure A3 is prepared and statistical tests are made to determine the significance of the assumed influences as compared to the experimental error.

SOURCE	SUM OF SQUARES	✓	MEAN SQUARE
C_1	$\frac{\sum(T_{1\dots})^2}{2NREPS} - \frac{(T\dots)^2}{4NREPS}$	1	$\frac{SSC}{\checkmark}$
E_j	$\frac{\sum(T_{\cdot j \cdot})^2}{2NREPS} - \frac{(T\dots)^2}{4NREPS}$	1	$\frac{SSE}{\checkmark}$
$(CXE)_{ij}$	$\frac{\sum(T_{ij\cdot})^2}{NREPS} - SSC - SSE - \frac{(T\dots)^2}{4NREPS}$	1	$\frac{SSI}{\checkmark}$
$\epsilon_{k(1j)}$	BY SUBTRACTION		
TOTALS	$\sum(D_{ijk})^2 - \frac{(T\dots)^2}{4NREPS}$	4NREPS-1	

Figure A3. An ANOVA table. The symbol ✓ represents degrees of freedom and NREPS is the number of replicates. For a complete explanation of the dot notation and other terminology, refer to Rickmers and Todd.

To determine whether or not the difference due to curves is significant, a statistical technique known as the F-test is used. The F-test is accomplished by forming a ratio of the mean square due to curves and the mean square due to error (assuming that curves are fixed), and comparing this value to a table value for the same number of degrees of freedom and for a particular value of alpha. Alpha is the chance you take of being wrong when you reject the null hypothesis (the null hypothesis here is that there is no difference due to curves). If the calculated F-test ratio exceeds the table value for the particular chosen value of alpha, then the null hypothesis is rejected and we say that we have evidence to suggest that there is a difference due to curves for that particular value of alpha. Conversely, if the F-test ratio is less than the table value, then we fail to reject the null hypothesis.

In "sliding ANOVA" these F-test calculations are made on adjacent curves at adjacent exposure levels throughout the exposure range (as indicated in Figure A1, this creates a 2 x 2 x NREPS factorial). The F-test values are then plotted against exposure at the midpoints of the particular exposure intervals involved. Table values for alpha risks of .05 and .01 are indicated in the plot as horizontal lines.

A drawback to "sliding ANOVA" is the prohibitive number of calculations which are necessary. To circumvent


```

REAL*4 MF
REAL*8 SSC(21,6),SSE(21,6),SSI(21,6),SSER(21,6),TMSER(21,6),CF(21,
B6)
DIMENSION Y(50),EXP(21),DENS(5,21,6),CCMP(6,21),DENSAV(5,21),SQDE
B(21,6),TC(21,6),TE(21,6),SQTC(21,6),SSTOT(21,6),FTESTI(21,6),FTEST
BE(21,6),FTESTC(21,6),TOT(21,6),SQI(21,6),SQTE(21,6),EEXP(21)
READ(5,18) MF,MSET
18 FORMAT(F4.1,I2)
DO 11 ISET=1,MSET
READ(5,3) (NNCURV,NNEXP,NNREP,EXPFAC,XSUB,IPP)
3 FORMAT(I2,I2,I2,F5.2,F4.2,I2)
NNE=NNEXP-1
NNC=NNCURV-1
DO 10 NREP=1,NNREP
DO 20 NCURV=1,NNCURV
READ(5,17) (DENS(NCURV,NEXP,NREP),NEXP=1,NNEXP)
17 FORMAT(11F5.2)
20 CONTINUE
10 CONTINUE
DO 30 J=1,NNEXP
DO 40 I=1,NNCURV
D=0.0
DO 50 NREP=1,NNREP
COMP(I,J)=DENS(I,J,NREP)+D
D=COMP(I,J)
50 CONTINUE
DENSAV(I,J)=COMP(I,J)/NNREP
40 CONTINUE
30 CONTINUE
DO 15 IN=1,NNE
DO 25 I=1,NNC
SQTT=0.0
DO 35 NREP=1,NNREP
SQDE(IN,I)= (DENS(I,IN,NREP))**2+(DENS(I,IN+1,NREP))**2 +SQTT+
R(DENS(I+1,IN,NREP))**2+(DENS(I+1,IN+1,NREP))**2
SQTT=SQDE(IN,I)
35 CONTINUE
25 CONTINUE
15 CONTINUE
DO 60 IN=1,NNEXP
DO 70 I=1,NNCURV
TE(IN,I)=COMP(I,IN)+COMP(I+1,IN)
TC(IN,I)=COMP(I,IN)+COMP(I,IN+1)
70 CONTINUE
60 CONTINUE
DO 80 IN=1,NNE
DO 90 I=1,NNC
TOT(IN,I)=TC(IN,I)+TC(IN,I+1)

```

FIGURE A4. Computer program which performs sliding ANOVA calculations and prints out the F-tests for both factors and the interaction.

```

SQTC(IN,I)=(TC(IN,I))**2+ (TC(IN,I+1))**2
SQI(IN,I)=(COMP(I,IN))**2+(COMP(I+1,IN))**2+(COMP(I,IN+1))**2+(COM
BP(I+1,IN+1))**2
SQTE(IN,I)=(TE(IN,I))**2+(TE(IN+1,I))**2
CF(IN,I)=(TOT(IN,I))**2/(4.*NNREP)
SSC(IN,I)=SQTC(IN,I)/(2.*NNREP)-CF(IN,I)
SSE(IN,I)=SQTE(IN,I)/(2.*NNREP)-CF(IN,I)
SSI(IN,I)=SQI(IN,I)/NNREP-SSC(IN,I)-SSE(IN,I)-CF(IN,I)
IF(SSI(IN,I).LT.0.0) SSI(IN,I)=0.0
SSTOT(IN,I)=SQDE(IN,I)-CF(IN,I)
SSER(IN,I)=SSTOT(IN,I)-SSC(IN,I)-SSE(IN,I)-SSI(IN,I)
TMSER(IN,I)=SSER(IN,I)/(4.*NNREP-4.)
IF(TMSER(IN,I).EQ.0.0) GO TO 43
FTESTI(IN,I)= SSI(IN,I)/TMSER(IN,I)
IF(TE(IN,I).EQ.TE(IN+1,I)) GO TO 33
FTESTE(IN,I)= SSE(IN,I)/TMSER(IN,I)
GO TO 34
33 FTESTE(IN,I)=0.0
34 IF(TC(IN,I).EQ.TC(IN,I+1)) GO TO 38
FTESTC(IN,I)= SSC(IN,I)/(TMSER(IN,I))
GO TO 90
38 FTESTC(IN,I)=0.0
GO TO 90
43 FTESTI(IN,I)=0.0
FTESTE(IN,I)=0.0
FTESTC(IN,I)=0.0
90 CONTINUE
80 CONTINUE
IF(IPP.EQ.1) GO TO 66
WRITE(6,53)
53 FORMAT('0',2X,'FTESTI',7X,'FTESTE',6X,'FTESTC')
DO 76 I=1,NNC
WRITE(6,54)(IN,FTESTI(IN,I),FTESTE(IN,I),FTESTC(IN,I),IN=1,NNC)
54 FORMAT(2X,12,2X,E10.3,2X,E10.3,2X,E10.3)
76 CONTINUE
DO 66 J=1,NNEXP
WRITE(6,119) (DENSAB(I,J),I=1,NNCURV)
119 FORMAT('0',2X,4F5.2)
66 CONTINUE
11 CONTINUE
STOP
END

```

FIGURE A4 (continued).

APPENDIX B

Silver Analysis

The procedure for determining the amount of silver per unit area involved removal of the silver and titration of the remaining halide with silver nitrate. Photographic emulsions are prepared in the presence of excess bromide in most cases so it is a limitation of this technique that the excess bromide cannot be distinguished from that which is present in molar amounts equivalent to the silver. The error should be small however.

Procedure

- 1) Fix six feet of the film in 500 milliliters of sodium cyanide solution (5 grams per liter).
- 2) Separate the solution from the film and take two additional 50 milliliter extractions.
- 3) Add two grams of zinc powder and heat to boiling.
- 4) Hold at boiling point ten minutes.
- 5) Cool, filter, and wash the precipitate.
- 6) Add 40 milliliters of glacial acetic acid and boil until only two-thirds the original volume remains.
- 7) Cool and titrate with 5×10^{-3} molar silver nitrate.

APPENDIX C

Nitrogen Burst Tank Variability and Design

To investigate the variability of the nitrogen burst tank, a factorial experiment was designed which could be easily evaluated by statistical methods. A total of 48 Cine Positive test strips were exposed through a 21 step Kodak #2 Step Tablet on a sensitometer and developed in DK-50 developer at 72° Fahrenheit (eight strips per run).

The factors were "runs" and "wells" (a well is one of a total of eight positions for film in the nitrogen burst tank). Analysis of variance (ANOVA) was used to evaluate the results. F-tests were made for "wells" and "runs" against the residual mean square to determine the statistical significance of the factors at each of several exposure levels.

The data tables and the ANOVA tables for the experiment are found in Table C1. The results show that the variability due to runs is quite significant whereas the variability due to wells is not significant at an alpha value of .05. The data suggests that the variability due to position is not as important as the necessity of maintaining consistent processing conditions for each replicate.

To determine the dependence of one source of experimental

TABLE C1. Nitrogen burst tank variability. An 8X6 factorial experiment and the statistical analysis (ANOVA) for various density levels; a) .41, b) .80, c) 1.25, d) 1.76, e) 2.25, f) 2.67. Alpha=.05.

	RUN#						
	1	2	3	4	5	6	TOTALS
1)	.43	.41	.40	.38	.42	.42	2.46
2)	.43	.40	.39	.39	.42	.41	2.44
3)	.42	.40	.39	.38	.42	.41	2.42
WELL# 4)	.43	.40	.39	.39	.42	.41	2.44
5)	.44	.40	.40	.39	.42	.41	2.46
6)	.43	.40	.39	.38	.42	.42	2.44
7)	.42	.40	.40	.39	.42	.42	2.45
8)	.42	.40	.39	.39	.41	.43	2.44
TOTAL	3.42	3.21	3.15	3.09	3.35	3.33	19.55

ANOVA TABLE

SOURCE	SUM OF SQUARES		MEAN SQUARES	F-RATIOS
RUNS	.010260	5	.002052	56.50 ***
WELLS	.0000198	7	2.83×10^{-6}	.08
RESIDUAL	.0012682	35	36.2×10^{-6}	
TOTALS	.011548	47		

*** statistically significant

$$\bar{D} = .41$$

$$s_{\text{wells}} = .0017$$

(a)

TABLE C1 (continued)

	RUN#						TOTALS
	1	2	3	4	5	6	
1)	.84	.80	.78	.76	.83	.82	4.83
2)	.84	.79	.77	.77	.82	.81	4.80
3)	.82	.78	.76	.77	.81	.81	4.75
WELL#4)	.83	.79	.77	.78	.82	.81	4.80
5)	.84	.79	.78	.77	.81	.81	4.80
6)	.82	.78	.78	.76	.82	.82	4.78
7)	.82	.79	.78	.78	.82	.82	4.81
8)	.82	.79	.78	.76	.83	.83	4.81
TOT	6.63	6.31	6.20	6.15	6.56	6.53	38.38

ANOVA

SOURCE	SUM OF SQUARES		MEAN SQUARE	F-RATIO
RUNS	.025742	5	.00515	90.50 ***
WELLS	.0006567	7	.000094	1.65
RESIDUAL	.001991	35	.000057	
TOTAL	.028390	47		

***statistically significant

$$\bar{D} = .80$$

$$s_{\text{wells}} = .00969$$

(b)

	RUN#						TOTALS
	1	2	3	4	5	6	
1)	1.31	1.25	1.22	1.20	1.29	1.26	7.53
2)	1.30	1.22	1.20	1.20	1.27	1.26	7.45
3)	1.28	1.23	1.20	1.21	1.26	1.26	7.44
WELL#4)	1.29	1.22	1.20	1.21	1.28	1.26	7.46
5)	1.30	1.22	1.23	1.21	1.26	1.27	7.49
6)	1.28	1.22	1.22	1.20	1.29	1.28	7.49
7)	1.28	1.23	1.23	1.20	1.28	1.27	7.49
8)	1.28	1.22	1.21	1.20	1.29	1.30	7.50
TOTAL	10.32	9.81	9.71	9.63	10.22	10.16	59.85

ANOVA TABLE

SOURCE	SUM OF SQUARES		MEAN SQUARES	F-RATIOS
RUNS	.053719	5	.01074	79.80 ***
WELLS	.001014	7	.00014	1.08
RESIDUAL	.004698	35	.00013	
TOTAL	.059431	47		

***statistically significant

$$\bar{D} = 1.25$$

$$s_{\text{wells}} = .012$$

(c)

	RUN#						TOTALS
	1	2	3	4	5	6	
1)	1.83	1.75	1.73	1.70	1.81	1.78	10.60
2)	1.81	1.72	1.72	1.71	1.78	1.77	10.51
3)	1.80	1.72	1.70	1.73	1.78	1.77	10.50
4)	1.79	1.72	1.69	1.73	1.80	1.77	10.50
5)	1.82	1.72	1.73	1.71	1.78	1.79	10.55
6)	1.80	1.71	1.71	1.73	1.81	1.79	10.55
7)	1.81	1.75	1.73	1.71	1.80	1.78	10.58
8)	1.80	1.73	1.72	1.72	1.81	1.80	10.58
TOT	14.46	13.82	13.73	13.74	14.37	14.25	84.37

ANOVA TABLE

SOURCE	SUM OF SQUARES		MEAN SQUARE	F-RATIO
RUNS	.070137	5	.01403	86.00 ***
WELLS	.001800	7	.00026	1.58
RESIDUAL	.005713	35	.00016	
TOTAL	.07765	47		

***statistically significant

$$\bar{D} = 1.76$$

$$s_{\text{wells}} = .016$$

(d)

	RUN#						TOTALS
	1	2	3	4	5	6	
1)	2.32	2.24	2.22	2.21	2.31	2.29	13.59
2)	2.30	2.22	2.23	2.21	2.29	2.26	13.51
3)	2.30	2.21	2.20	2.21	2.28	2.28	13.48
WELL# 4)	2.30	2.22	2.17	2.21	2.30	2.26	13.46
5)	2.31	2.21	2.23	2.21	2.30	2.28	13.54
6)	2.30	2.21	2.20	2.21	2.30	2.28	13.50
7)	2.31	2.23	2.23	2.20	2.30	2.30	13.57
8)	2.29	2.22	2.22	2.22	2.31	2.28	13.54
TOTAL	18.43	17.76	17.70	17.68	18.39	18.23	108.19

ANOVA TABLE

SOURCE	SUM OF SQUARES		MEAN SQUARES	F-RATIOS
RUNS	.079236	5	.015847	126.00 ***
WELLS	.002298	7	.000328	2.60
RESIDUAL	.004416	35	.000126	
TOTAL	.08595	47		

***statistically significant

$$\bar{D} = 2.25$$

$$s_{\text{wells}} = .018$$

(e)

	RUN#						TOTALS
	1	2	3	4	5	6	
1)	2.75	2.64	2.62	2.65	2.74	2.70	16.10
2)	2.73	2.65	2.66	2.62	2.71	2.66	16.03
3)	2.72	2.61	2.62	2.66	2.69	2.70	16.00
WELL# 4)	2.73	2.62	2.66	2.60	2.72	2.67	16.00
5)	2.75	2.64	2.63	2.66	2.73	2.70	16.11
6)	2.75	2.63	2.62	2.63	2.68	2.68	15.99
7)	2.72	2.64	2.64	2.62	2.70	2.72	16.04
8)	2.72	2.64	2.66	2.62	2.74	2.65	16.03
TOT	21.87	21.07	21.11	21.06	21.71	21.48	128.30

SOURCE	SUM OF SQUARES		MEAN SQUARE	F-ratio
RUNS	.078792	5	.015758	40.00 ***
WELLS	.002242	7	.000320	.82
RESIDUAL	.013758	35	.000393	
TOTAL	.094792	47		

***statistically significant

$$\bar{D} = 2.67$$

$$s_{wells} = .0179$$

(f)

variability on the density level for these particular processing conditions, the estimate of the standard deviation attributable to "wells" only was calculated (by taking the square root of the mean square due to "wells"). These results were plotted in Figure 2 and the indication was that the variability was quite dependent on the density. This fact contributed to the rationale behind the "sliding ANOVA" technique described in Appendix A.

The schematic in Figure C2 gives a general description of the nitrogen burst tank and the film carrier. The film carrier utilized rubber bands for mounting the film thereby providing a lengthwise tension on the film that would hold it firmly and flat. The tank was designed to hold a maximum of approximately nine-tenths of a liter of developing solution. The bursts were created by forcing nitrogen gas through a set of holes approximately .016 inch in diameter that were positioned inside the tank in a design which was conducive to uniform agitation. The burst duration and interval were controlled by a Kodak Intermittant Gaseous Burst Regulator.

This model had a unique valve design which minimized developer back-up which tends to occur after each burst with other models. The apparatus belongs to Rochester Institute of Technology and was constructed by Mr. Richard Norman as a project of the Photographic Science Department.

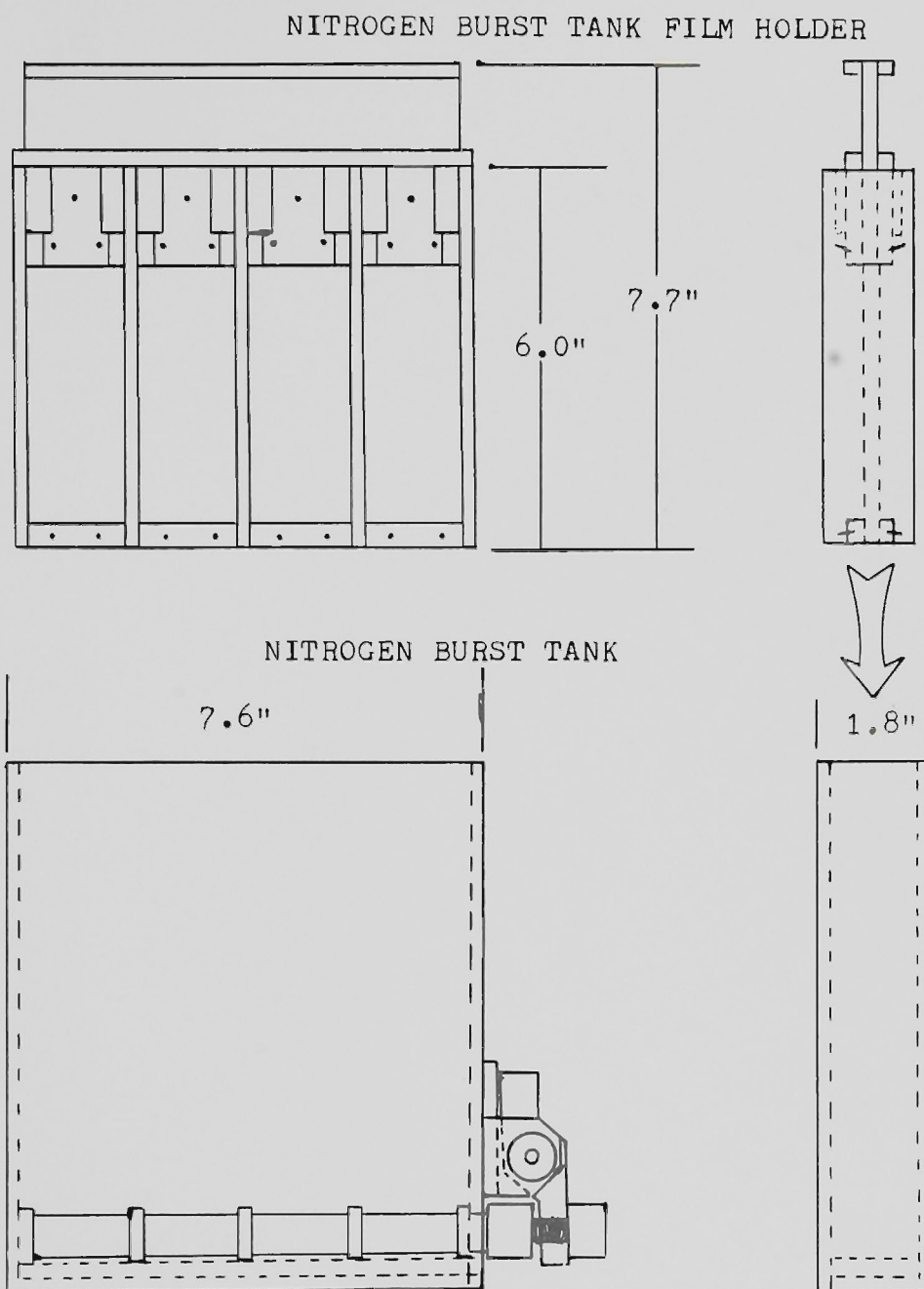


FIGURE C2. General schematic of the nitrogen burst tank and the nitrogen burst tank film carrier.