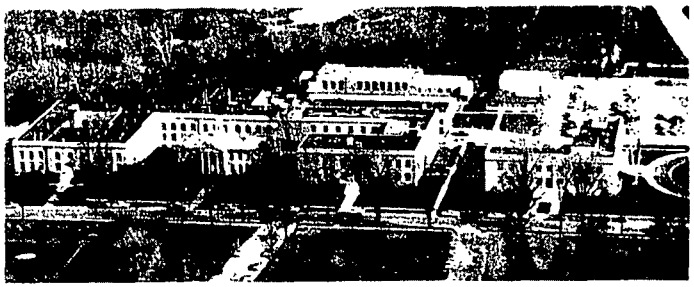

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

DEVELOPMENT OF A MANUFACTURING PROCEDURE FOR LOW-LITHIUM, LOW-URANIUM CONTENT FILTER PAPER

Project 3101-1

Report Sixteen

A Status Report

to

DEPARTMENT OF THE AIR FORCE
1155th TECHNICAL OPERATIONS SQUADRON (HQ. COMD.)
McCLELLAN AFB, CALIFORNIA

January 15, 1975

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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DEVELOPMENT OF A MANUFACTURING PROCEDURE FOR LOW-LITHIUM, LOW-URANIUM CONTENT FILTER PAPER

SUMMARY

Two lots of 19-inch squares of IPC-1478 paper, Series N, were purified by leaching in two cycles with ammonium carbonate and hydrofluoric acid. Kronisol at the rate of 30% by weight, based on the airdry paper, was applied from a paint sprayer. The lithium levels were approximately double, 2.5-3.5 ng Li/g of paper, those expected for paper purified by the procedure as described. Work is under way to improve the procedure.

Selected samples of pulp and paper were analyzed by emission spectrography. The purification procedure generally removed 85-91% of the ash (by muffle furnace at 550°C). The removal of sodium was 84-94%, similar to that of lithium as determined by mass spectrometry at McClellan AFB-MCL-C. The removal of manganese was similar in efficiency to that of uranium. These observations may be helpful in the design of experiments which will enable the Institute to monitor some of the results of future purification attempts. Thus, sodium and manganese may be considered as indicators for lithium and uranium, respectively.

A copy of a memorandum is included on Project 3101-1 concerning the pilot-plant tests conducted at Knowlton Brothers, Watertown, N.Y., in August, 1974.

RESULTS AND DISCUSSION

PURIFICATION OF IPC-1478, SERIES N PAPER

The purification of two lots of 120 sheets of 19-inch squares of IPC-1478, Series N paper was completed. In order to reduce the lithium level as far as possible, the purification cycle was repeated on two lots. These were then treated with Kronisol by means of an electric paint sprayer[1]. On December 3, 1974, Jack Phelps reported by telephone that the two lots (Samples 376 and 378, Table I) had retained amounts of lithium in excess of the expected low levels of < 2 ng Li/g. The source of lithium appeared to be the Kronisol, either through exposure during the spraying or possibly from contaminated Kronisol, inasmuch as the unsprayed paper contained < 1.5 ng Li/g.

On December 30, 1974, Jack Phelps reported that the Kronisol used on Samples 376 and 378 contained 1.29 ng Li/ml, a larger amount of lithium than is usually found in this material, and the application of 30% by weight to the purified paper would add about 0.4 ng Li/g to the finished paper. However, the lithium content of the finished paper, without contamination by exposure or from the spraying equipment, would be essentially unchanged by comparison with the untreated paper (Table I, calculated values). Thus, Samples 376 and 378 would appear to have received additional lithium either from the spraying equipment or through exposure to laboratory dust during the spraying step.

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[1]A new appliance, purchased from a local hardware store, was the Burgess Paint Sprayer, Model VS-860.

TABLE I

LITHIUM CONTENTS OF IPC-1478 PAPER, SERIES N
AFTER PURIFICATION AND TREATMENT WITH KRONISOL[a]

Sample No. 3101-	Uranium 8/5	Uranium ng/g		Lithium, ng Li/g	Remarks
					From Roll No. 11-9;
368				1.43	after 1st cycle
376	131	0.119	A	3.87	
	130	0.071	B	2.71	after 2nd cycle; Kronisol added
		(calcd.		1.40)[b]	
					From Roll No. 11-7;
370	125	0.068		1.34	after 1st cycle
378	130	0.205	A	2.60	
	129	0.084	B	2.08	after 2nd cycle; Kronisol added
		(calcd.		1.33)[b]	
					From Roll No. 11-4;
372				1.36	after 1st cycle
					From Roll No. 11-1;
374	134	0.090		1.06	after 1st cycle
392				1.29 ng/ml	Kronisol, control
				ng/ml	
369				0.008	Deionized process water
371				0.006	
373				0.009	
375				0.004	
377				0.005	
379				0.011	

[a]See Experimental, for details. These data were reported by letter dated January 7, 1975, from Jack Phelps to E. E. Dickey.
[b]Based on 1.00 g of finished paper composed of 0.77 g of purified paper and 0.23 g of Kronisol.

In order to test the premise that the spraying equipment may have contaminated the Kronisol, one lot of the 19-inch squares was treated with Kronisol by means of a perforated, polyethylene bottle applicator. The sample was submitted for analysis under No. 409 on December 20, 1974.

ANALYSES BY EMISSION SPECTROGRAPHY

The mineral contents of selected samples of IPC-1478 paper and Hercules pulp, PS-57, from which the paper was manufactured, were determined by emission spectrography. The results, summarized in Table II, show that 85-91% of the mineral (ash components) was removed in the purification process. The increased amounts of sodium and calcium of the paper (No. 294) compared with the pulp (No. 001) are believed to be due in part to the chemicals used in treating the water in the mill at Watertown, N.Y. The increase in iron and copper may be due to the equipment and plumbing. The increases in aluminum and silicon were not marked, and most other elements were not changed significantly.

The purified samples (No. 279, 281, and 341, respectively) retained proportionately larger amounts of the main ash components than of the minor elements. Thus, sodium, calcium, iron, silicon, and phosphorus were especially persistent, and readily account for the bulk of the ash in the purified pulp and paper.

The uranium and lithium data for these samples were reported previously (1), but are included in Table II for comparison. It may be noteworthy that the efficiency of the removal of lithium (96%) was approximately the same as that of sodium (94%) for the IPC-1478 paper. The efficiency for the removal of lithium (84%) from the pulp was lower than for the paper, but the total amount was approximately one-tenth of that of the paper. The efficiency of sodium removal (84%) was similar to that of lithium.

The removal of uranium was accomplished at efficiencies of 91-96%, similar to the removal of manganese. This observation, together with the

TABLE II

ANALYSIS OF IPC-1478 PAPER, SERIES N, AND HERCULES PULP, PS-57, BY EMISSION SPECTROGRAPHY

The samples were ashed at 550° in a muffle furnace

Sample	IPC-1478 Paper, Series N, Roll No. 22			Hercules Pulp, PS-57			
No. 3101-	294, control	279, 281 purified	Residue After Purification, %	001, control	341, purified	Residue After Purification, %	Chemically Treated[c]
Amount analyzed, g	4.68[a]	6.60[a]		13.70	12.15		4.15
Yield of ash, %	0.11	0.017	15	0.056	0.0051	9	0.13
Elements by Emission Spectrography, ppm							
Aluminum	14	2.2	16	9.8	0.54	5.5	3.4
Barium	0.58	0.15	26	0.23	0.047	20	0.20
Boron	0.57	0.074	13	0.056	0.13	230	1.4
Calcium	128	32	25	99	8.6	8.7	18
Chromium	0.16	0.096	60	0.11	0.029	26	0.28
Copper	4.3	0.42	9.8	1.4	0.40	29	7.5
Iron	18	6.8	38	5.2	1.5	29	9.9
Lead	0.23	0.12	52	0.16	0.058	36	0.68
Magnesium	11	3.6	33	11	1.8	16	520
Manganese	0.94	0.040	4	0.15	0.016	11	0.35
Phosphorus	8.8	3.5	40	4.0	1.6	40	--
Silicon	22	7.2	33	18	2.4	13	50
Silver	0.0089	0.0089	100	0.0052	0.0024	46	--
Sodium	250	16	6.4	86	14	16	32
Titanium	0.64	0.41	64	0.32	0.16	50	0.78
Lithium, ng/g[b]	23.4	1.03	4	2.37	0.37	16	--
Uranium, ng/g[b]	0.64	0.06	9	1.26	0.05	4	--

[a] These samples were ashed without removing the scrim. At McClellan AFB the scrim is removed before samples of paper are analyzed.

[b] Data for lithium and uranium from Project 3101, Report Seven, p. 7 and Report Fourteen, p. 28, 31 (No. 280).

[c] The Hercules pulp was treated with 1% magnesium carbonate and 5% sodium hydroxide (based on the weight of the pulp) at 120° for one hour, washed with deionized water and dried.

observed similarity between lithium and sodium, may be helpful in the design of experiments which will enable the Institute to monitor some of the results of purification attempts. Thus, sodium and manganese may be considered as indicators for lithium and uranium, respectively.

It was observed at the McClellan Laboratory that the ash formed from the Series N paper was brown colored, whereas the ash from the pulp samples was white. The spectrographic analyses failed to reveal components which account for the dark color; no further work has been planned to search for the cause of the color.

In the last column in Table II are listed the components in a sample of Hercules PS-57 pulp which had been heated for one hour at 120° with magnesium carbonate and sodium hydroxide, washed with water and dried.[2] The results indicated that even without an acid treatment, the levels of aluminum, calcium, and sodium were reduced relative to the starting material (001). Magnesium, which was probably absorbed on the pulp fibers, was the most persistent element under the conditions of the experiment. Also, the increased levels of silicon, boron, iron, and copper may be due to contact with glass and stainless steel apparatus. In general, the behavior of the pulp components in this experiment was consistent with predictable behavior, and no further experiments of this type are planned.

[2]PS-57 pulp was used as "pure" cellulose on a project (IPC) which supplied the data in Table II, Column 8.

PILOT PLANT STUDIES, KNOWLTON BROTHERS CO., AUGUST, 1974

IPC-1478 paper, Series N, was made by Knowlton Brothers Co., Watertown, N.Y., in October, 1973. Subsequently, the lithium content was found to be approximately 20 ng Li/g, a level too high for use in most field applications. In order to try to determine the reason(s) for the lithium in the Series N paper, pilot-plant experiments were designed by personnel of the McClellan AFB, MCL-C in cooperation with Knowlton Brothers. The tests were conducted August 11-14, 1974 (see Appendix I).

The results of these tests support the premise that the high lithium level of the Series N paper was due to the unexpectedly high levels of lithium in the process water. Details of the experiments and of the results were recorded at McClellan AFB, MCL-C, under the supervision of Jack Phelps, Chief Mass Spec Chemistry Unit, who may be consulted for further information.

FUTURE WORK

1. Additional lots of Series N paper in 19-inch squares are in the process of purification.

2. Experiments are under way to evaluate more fully the role of process water in the level of lithium in IPC-1478 paper.

3. The possible role of fines in the retention of lithium is under investigation.

EXPERIMENTAL

365. PURIFICATION OF SERIES N PAPER, ROLL 22[3]

An amount of 35 sheets, 20-inches square, was cut by hand from Roll No. 22 of the IPC-1478, Series N paper. Several sheets of the Hercules PS-57, dry-lapped pulp were stacked with the paper, and the stack was leached by percolation with the following solutions.

8 liters	0.1M hydrofluoric acid
10 liters	deionized water
8 liters	0.1M ammonium carbonate
10 liters	deionized water
8 liters	0.1M hydrofluoric acid
20 liters	deionized water.

The stack was pressed under a rubber sheet at reduced pressure (approximately 10 inches of mercury produced by a water aspirator pump), and dried in a stream of filtered air at room temperature.

Kronisol, 362 g (30% based on 1206 g of the dry, purified paper), was poured as evenly as possible onto the stack of purified paper. After standing for two hours, the bottom sheets were interleaved with the top sheets and the stack was allowed to stand for 48 hours. The sheets were then weighed individually and restacked with the sheets containing the least Kronisol placed in contact with those containing the largest amount of Kronisol. In this order the stack was assigned the number 365 and was shipped to McClellan AFB. Representative analytical data are listed in Report Fifteen, Table I, p. 4.

[3]This procedure was omitted unintentionally from Report Fifteen.

368-374. PURIFICATION OF SERIES N PAPER

Stacks of 19-inch squares, 120 sheets from each of four rolls, were leached by percolation in succession with the following solutions in each of two cycles.

15 liters	0.1M hydrofluoric acid
15 liters	deionized water
15 liters	0.1M ammonium carbonate
15 liters	deionized water
15 liters	0.1M hydrofluoric acid
55 liters	deionized water (free of acid to Congo Red paper)

The stack was pressed under a rubber sheet by a partial vacuum (water aspirator pump) to a consistency of 20-25% and the sheets were dried in a stream of filtered air at room temperature.

Kronisol was applied from a small paint sprayer at a rate of 30% based on the weight of the untreated, airdry paper. Analytical samples and the finished paper were assigned the numbers as shown in Table I.

LITERATURE CITED

1. Project 3101, Report Seven, August 22, 1973, p. 7, and Report Fourteen, September 30, 1974, p. 28, 31.

THE INSTITUTE OF PAPER CHEMISTRY

Edgar E. Dickey
Senior Research Associate
Division of Natural
Materials & Systems

Irwin A. Pearl
Group Coordinator
Division of Natural
Materials & Systems

Department of the Air Force
1155th Technical Operations Squadron (Hq. Comd.)
McClellan AFB, California
Project 3101-1

APPENDIX I

PROJECT 3101-1 MEMORANDUM.
CONFERENCE AT KNOWLTON BROTHERS CO., WATERTOWN, N.Y.,
AUGUST 11-14, 1974. PILOT-PLANT TESTS

Summary

The first-hand observation of the pilot plant tests, and the discussions with personnel from Knowlton Brothers and from McClellan Air Force Base were very helpful in our understanding of the nature and origin of uranium and lithium contents of IPC-1478 paper.

1. The uranium contents of IPC-1478 papers resulting from the papermaking process are due mainly to the levels of uranium in the pulp and, to some degree, in the process water.

2. The relatively high lithium content of Series N paper appears to have come mainly from the lithium carried (on the sheet) by the process water into the drying step.

3. The relatively high lithium content of the process water (five times higher than the Watertown city water) for the Series N paper has not been accounted for, but may have intruded from lubricants (for the machinery) or from unknown residues in the water system.

4. Pulp fines may carry a disproportionately large fraction of the lithium retained by pulp or paper. Additional experiments with pulp fines may be performed on Project 3101-1.

5. More information about the mineral content of IPC-paper before and after purification will be obtained at the IPC through ashing and emission spectrography.

6. One possible scheme to reduce the amounts of mineral components could involve a device just ahead of the couch roll to displace the process water with deionized water.

7. In addition to conventional papermaking, dry-forming of the sheet may be considered in the development of ultra-low levels of mineral components in filter paper.

8. The application of Kronisol by roll applicator is not suspected as a significant source of lithium.

Introduction

In general accord with the plan as stated in a memorandum dated August 6, 1974, from E. Dickey to Swanson, et. al., I arrived in Watertown on Sunday, August 11, in the late afternoon. Jack Phelps and Sgt. Tom Nibarger, McClellan AFB, MCL-C, arrived after midnight on the same day.

On Monday morning, August 12, at the motel we reviewed the objectives and the plans for the tests to be made in the pilot plant at Knowlton Brothers. An appointment was arranged (by Jack Phelps) for us to meet with Dr. Grant Rauscher at 1:30 p.m. We learned that the pilot plant was being cleaned and readied for the tests which were planned for Tuesday and Wednesday, August 13 and 14.

In the course of our conversations on Monday afternoon, the plans for the tests were reviewed in some detail. It was apparent that the main question to be answered was: "Why is the lithium content of the Series N paper so high?" [The lithium contents of previous lots of the IPC-1478 paper were 4-8 ng Li/g, whereas, Series N paper is approximately 20 ng Li/g.] The pilot plant tests were designed to compare the effects of reprocessed mill water with those of Watertown city water in making the paper. Samples of water collected in October, 1973 during the making of Series N paper analyzed:

ng/ml	city water	mill water after clarification
Lithium	0.8	3.5
Uranium	0.005	0.007

Thus, if the water content of the sheet entering the drier was 75-80%, the city water would have left 3.2-4.0 ng Li/g of paper and the mill water would have left 14-17.5 ng Li/g in the sheet. In the case of the mill water, these amounts could readily account for the final values of ca. 20 ng Li/g in Series N paper.

Pilot Plant Tests

Five tests were planned whereby IPC-1478 paper would be made in the pilot plant as follows:

1. Mill water at pH 9.5; white water recirculated;
2. Mill water at pH 4.1; white water recirculated;
3. City water at pH 9.5; white water discarded;
4. City water at pH 9.5; white water recirculated;
5. City water at pH 9.5; white water recirculated; quantity of paper produced for use at McClellan AFB.

The equipment was thoroughly washed between each test to reduce the cross-contamination of samples. In the first four tests, the run was continued until a steady state had been reached in making paper at 90 lbs/3000 sq. ft., then analytical samples of water and paper were collected and the test was stopped. Upon reaching the correct basis weight in test no. 5, several rolls of paper were collected. This paper will be saturated eventually with Kronisol and used at McClellan.

In the process as used in these tests, 15 lbs. of dry-lapped pulp (Hercules PS-57) was dispersed in a Valley beater to which 80 ml of concentrated ammonium hydroxide (28-29% NH_3, AR) and 25 g. of ammonium carbonate were added. At the headbox, the pulp was diluted with water for a total of 1800 lbs. of water to a consistency of 0.8% at pH 9.5. The sheet was formed

on scrim at 19.3 ft./min. The sheet left the wire at the couch roll (2.5 in. Hg. reduced pressure) and was carried on a felt without pressing to the drier section which consisted of a gas-fired infrared unit followed by eleven 14-inch, steam-heated rolls.

Although the web was pressed at no point, the tension on the web as it passed over the drier rolls determined the final smoothness and density of the sheet. There was some concern that the tension should be maintained at a minimum to prevent any tendency to increase the density of the sheet and thereby reduce its air-permeability. The air-filtration characteristics and particle retention ability will be tested on the Air Force tester (IPC design) housed at Knowlton Brothers.

Possible Sources of Lithium

In reviewing the possible sources of lithium which could raise the lithium content of mill water by factors of four or more over the city water, very few promising ones were found.

In recirculated mill water lithium may be leached from the concrete floor underneath the machine and from the piping, but these are considered to be a minor source.

Because the lithium salts of fatty acids are known to be added to some lubricants, samples of oil and grease were obtained for lithium analysis. Other real sources, if any, remain hidden. If the lithium contents of the several samples from the pilot plant tests are inexplicably high, an intensive search will be started to find the source of the lithium.

Possible Role of Fines

One of the tests performed by Capt. Grosso involved the white water from the Series N papermaking operation in October, 1973. A sample of the water was filtered through pads of L-series paper (4.2 ng Li/g), and the paper was dried and analyzed. The lithium contents were then 34-70 ng Li/g. These results together with the results of an experiment on Project 3101 (Report Ten, p. 12) support the probability that pulp fines concentrate the lithium. To understand better the possible role of fines in the retention of lithium in IPC-1478 paper, further experiments are being considered. A closely related experiment will attempt to determine whether or not the ion-exchange capacity of the pulp may be sufficient to remove lithium from process water. Previous experiments with lithium-6 (Report Seven, p. 16) indicated that most, if not all, lithium may be exchangeable.

Other Factors Affecting the Lithium Content

IPC-1478 filter paper, Series-L, was made from pulp which had been specially washed by Hercules, Inc., and the lithium and uranium contents of the L-series were the lowest of any of the lots made by Knowlton Brothers. In addition to the use of specially purified pulp, the process water was taken from the Black River instead of the Watertown city water as was the case for the Series-N paper. Also, the process water was filtered through anthracite and diatomaceous earth and the white water was not recycled. The use of the anthracite and diatomaceous earth filters has been discontinued, and the white water for the Series-N paper was recycled.

Although these differences in the manufacturing processes for Series-L and Series-N may contribute to the markedly higher level of lithium in the Series-N paper, the main source of the lithium remains hidden.

Filtration and Retention Tests

IPC-1478 paper, Series-N, had been purified on Project 3101, treated with Kronisol, and sent to McClellan AFB as sample 3101-350 (see Report Thirteen, p. 5). Several specimens of this lot of paper were subsequently sent to Knowlton Brothers by the McClellan Laboratory for air filtration and retention tests. The Laboratory at Knowlton Brothers applied Kronisol to the specimens before testing without knowing that Kronisol had been added at the IPC. The results are listed on the attached data sheet. As interpreted by Dr. Rauscher and Jack Phelps, the performance showed that the purification process had not changed the required properties of the paper.

Ash Content and Composition of IPC-1478 Paper

The analytical procedure used by McClellan AFB, MCL-C includes no measure of total ash. Consistent with tentative plans outlined previously (see Memo dated June 21, 1974, Dickey to Swanson, et al.) several types of paper, purified and unpurified, will be submitted to the IPC Analytical Group for (a) total ash and (b) elemental analysis by emission spectrography. One of the questions which may be answered in these studies is concerned with the brown color of the ash from Series-N paper in contrast to the ashes of other papers which are white.

Miscellaneous Observations and Comments

1. One run of paper on the pilot plant was made at pH 4.1 (measured at the headbox) obtained by the addition of hydrochloric acid. The pH was chosen to test the effect of acid on the retention of lithium by the paper. The performance apparently was the same as at pH 9.5 except that the white water was essentially free of fines. This effect was unexpected and may signal other differences in the properties of the sheet.

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2. Because of the sensitivity of the uranium and lithium contents of IPC-1478 paper to water quality, Dr. Rauscher suggested that forming the sheet in air instead of water should favor the production of paper with low levels of impurities. Such methods have been considered in past discussion and rejected because of the major effort required to form and bond a satisfactory sheet. However, the possibilities for the production of a satisfactory filter paper with very low levels of impurities by an air-forming process are real and may appear eventually more practical than at present.

3. The crew on the pilot plant consisted of Paul Nutting, pulpman; Bob Campaney, machine tender; and Don DeForde, pilot machine supervisor. Dr. Grant Rauscher was responsible for planning the work and the main course of the tests. The crew worked together very effectively.

4. In a conversation with Dr. Rauscher we raised the possibility of installing a device just before the couch roll which would preserve the formation and provide sufficient deionized water to displace the process water from the sheet as it passed over the couch roll. Such a device should remove most of the dissolved impurities which would otherwise be dried on the paper. The sheet passes to the drier section at approximately 76% water so that process water at 4 ng. Li/ml. alone would carry 12 ng. Li/g into the finished sheet. A quick washing step with "pure" water at the couch roll should remove most of this load of lithium.

5. Kronisol is applied by a roll applicator (saturator). The machine is used for many types of specialty papers with exposure to many types of chemical materials. However, the equipment appears to be cleaned readily and is probably not significant in adding impurities to the finished IPC-1478 paper. Kronisol, itself, is usually low-to-insignificant in its lithium content.

The results of these tests should provide at least a partial answer to the question, "Why is the lithium content of Series-N IPC-1478 paper abnormally high?"

EED/ctb
Attachment

GRADE 107 IPC # 3101-350 IPC 1-18 POST-TREATED SAMPLES K-24% KROMUSIL 8/9/74

SAMPLE NO. OR LOT NO.	PRESSURE DROP INCHES OF WATER LEFT MAN 1.25" ORIFICE	AIR VELOCITY FT/MIN. THRU SPECIMEN	PRESSURE DROP INCHES OF WATER ACROSS SPECIMEN RIGHT MAN.	UPPER CELL CLEAN AIR * A	UPPER CELL DUST LADEN AIR NO SPECIMEN B	LOWER CELL CLEAN AIR * C	LOWER CELL DUST LADEN AIR NO SPECIMEN E	UPPER CELL DUST LADEN AIR WITH SPECIMEN G	LOWER CELL DUST LADEN AIR WITH SPECIMEN F	RETENTION %
K 1	40	2150	30	32	93	32	93	96	34	96.9
K 3	36	2040		32		32			34	96.9
7	38	2100		33		32			34	96.9
K 8	33	1950		33		33			35	96.9
9	40	2150		33		33			35	96.9
K 10	36	2040		32		33			36	96.9
13	42	2200		33		33			35	96.9
K 18	40	2150		32		33			35	96.9

* Due to contamination of air, paper No. IPC 1478 (or equivalent) should be inserted in sample holder.