Technical Report No. IRL 1111

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

LUNAR SAMPLE ANALYSIS PROGRAM

THE STUDY OF TERRESTRIAL AND EXTRATERRESTRIAL PORPHYRINS

IN ASSOCIATION WITH AMINO ACID COMPOUNDS

Proposal No. 05-020-(296)

TITLE: SEARCH FOR PORPHYRINS IN LUNAR FINES FROM APOLLO 11 AND 12

By

B. Halpern and G. W. Hodgson

August 15, 1970

Principal Investigator: B. Halpern

Co-Investigator: G. W. Hodgson

FINAL REPORT

Prepared under Contract No. NAS9-9439

Department of Genetics

Stanford University School of Medicine

Stanford, California 94305

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Manned Spacecraft Center
Lunar Receiving Laboratory
Houston, Texas

FACILITY FORM 602

N71-11067 (ACCESSION NUMBER)	(THRU)
133 (PAGES)	G3 (CODE)
CR-108671 (NASA CR OR TMX OR AD NUMBER)	04 (CATEGORY)

CR-108671

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ABSTRACT

Evidence for porphyrins was obtained in Apollo 11 and 12 lunar fines samples. The pigments from samples collected near the lunar lander were probably due to contamination by rocket exhaust products. A porphyrin-like pigment ($\sim 5 \times 10^{-5}$ μg/g) was also found in an Apollo 12 sample, which had been collected at a point well removed from the lunar landing site.

SEARCH FOR PORPHYRINS IN LUNAR FINES FROM APOLLO 11 AND 12

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SUMMARY

Lunar fines from Apollo 11 and 12 samples contain porphyrin-like pigments as indicated by fluorescence spectrometry and analytical demetallation. The pigments from close in samples of Apollo 11 and 12 were probably products of rocket combustion which were introduced during landing of the lunar module. Porphyrin-like pigments were also found in a sample of lunar soil collected on the Apollo 12 mission at a sampling point well removed from the lunar landing site. Fluorescent demetallation analysis indicated that the pigments were present as metal complexes. Abundance was estimated to be 5×10^{-5} μg/g.

INTRODUCTION

The Oparin-Haldane hypothesis postulates that organic molecules were synthesized by the action of various forms of energy on primeval atmospheres. An orderly process of chemical evolution led to the living organism of today. The lunar samples provide us with an opportunity of examining this postulate in the case of samples outside the earth.

Under NASA grant NAS9-9439 we have tried to establish answers to the following questions:

1. Are porphyrins present in the Apollo 11 and 12 samples?
2. If porphyrins are present, can they be identified as biogenic pigments.

The prior art, scope, experimental techniques used and the significance of the material presented are summarized in the attached publications and reports.

SEARCH FOR PORPHYRINS IN LUNAR FINES FROM APOLLO 11 AND 12

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ABSTRACT

Evidence for porphyrins was obtained in Apollo 11 and 12 lunar fines samples. The pigments from samples collected near the lunar lander were probably due to contamination by rocket exhaust products. A porphyrin-like pigment ($\sim 5 \times 10^{-5}$ μg/g) was also found in an Apollo 12 sample, which had been collected at a point well removed from the lunar landing site.

Publications

1. Search for Porphyrins in Lunar Dust. By G. W. Hodgson, E. Peterson, K. A. Kvenvolden, E. Bunnenberg, B. Halpern and C. Ponnamperuma. Science 167, 763-5 (1970).

2. Carbon Compounds in Lunar Fines from Mare Tranquillitatis II. Search for Porphyrins. By. G. W. Hodgson, E. Bunnenberg, B. Halpern, E. Peterson, K. A. Kvenvolden and C. Ponnamperuma. Geochimica et Cosmochimica Acta: Proceedings of the Apollo 11 Lunar Science Conference II, 1829 (1970).

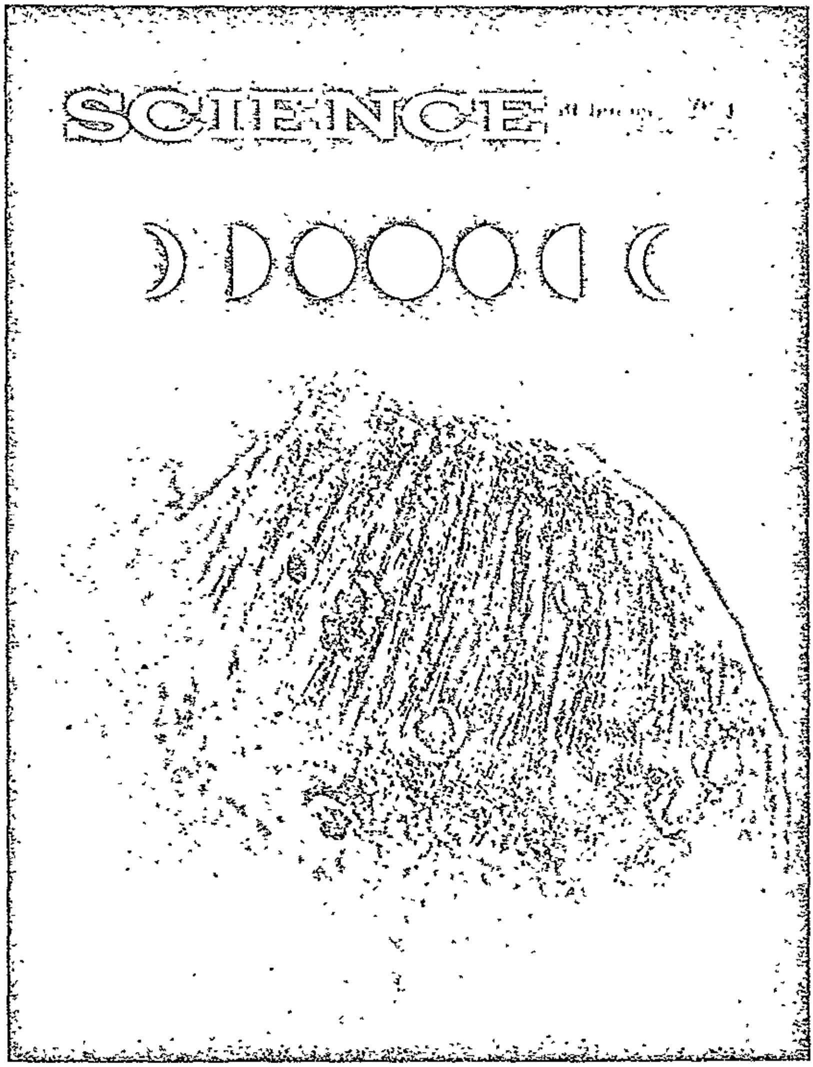
3. Lunar Pigments: Possible presence of Porphyrins in Apollo 12 Sample. By G. W. Hodgson, E. Peterson, K. A. Kvenvolden, E. Bunnenberg, B. Halpern and C. Ponnamperuma. Submitted to Science (1970).

4. Report on the Analysis of an Organic Extract of the Lunar Sample for Metalloporphyrins by Magnetic Circular Dichroism. E. Bunnenberg and W. E. Reynolds.

Reprinted from
30 January 1970, Volume 167, pp. 763-765

SCIENCE

Apollo 11 Lunar Science Conference



Search for Porphyrins in Lunar Dust

Gordon W. Hodgson, Etta Peterson, Keith A. Kvenvolden,
Edward Bunnenberg, B. Halpern and C. Ponnamperuma

Search for Porphyrins in Lunar Dust

Abstract. *Evidence for porphyrins was obtained in the Apollo 11 bulk sample of lunar dust by fluorescence spectrometry and analytical demetallation. The indicated porphyrins showed major fluorescence excitation at 390 nanometers. Abundance was about* 10^{-10} *gram of porphyrin per gram of dust. Similar pigments were found in exhaust products from tests of a lunar descent engine. The similarity of results suggests that most if not all of the indicated porphyrin aggregate of the lunar sample probably was synthesized from rocket fuel during the landing of the lunar module. These compounds may be the product of a novel high-temperature synthesis of cosmochemical interest.*

The present study was undertaken to determine whether porphyrins, tetrapyrrole organic pigments, were present in the Apollo 11 bulk sample and whether their presence in the sample was indicative of a biological origin (*1*). The results of the analyses show that pigments with spectral and chemical characteristics resembling porphyrins are present in the lunar bulk fines, but it appears that the compounds may have been introduced by the lunar descent rocket engine fueled with unsymmetrical dimethylhydrazine. Thus, while the analyses reported here evidently failed to reveal porphyrins which were unequivocally indigenous, the findings suggest that the porphyrins can perhaps be synthesized through a novel reaction involving simple compounds containing carbon, nitrogen, hydrogen, and oxygen. The pigments have also been detected in experiments simulating primitive (prebiotic) planetary conditions (*2*), and similar compounds evidently exist extraterrestrially, because porphyrins have been detected in a number of samples of carbonaceous chondrites (see *3*).

The analyses reported here are part of a comprehensive analytical program established by the Chemical Evolution Branch of the NASA Ames Research Center for the examination of all organic matter in the returned lunar samples (*4*). The group arranged to pool samples of lunar dust received by the principal investigators involved in the program. The particular sample discussed here was designated "10,086 bulk A fines" by the Lunar Receiving Laboratory.

Prior to receipt of the lunar samples, a simulation experiment was carried out on a sample of the Pueblito de Allende meteorite. Although analyses on a number of specimens of this meteorite showed porphyrins to be present in very small amounts (*5*), no porphyrins were detected in the particular sample used in the control run, and the results were substantially the same for a blank of Ottawa sand which had been fired at 1000°C for 48 hours.

The overall analytical procedure for the lunar sample is described by Ponnamperuma *et al.* (*4*). The lunar dust (54.6 g) was extracted directly with benzene-methanol (9:1), and 23 percent of the extract was made available for porphyrin analysis.

On concentration of the solution to a volume of 1 ml, weak emission bands at 600 and 630 nm for excitation at 400 and 425 nm (Turner 210 spectrofluorometer) appeared. Clear-cut excitation peaks for emission at 600 nm were observed at 390 and 455 nm, the latter being much more intense. Corresponding readings for the blank of Ottawa sand showed only a low background and no discernible peaks. Absorption spectrometry (Cary 14, 0 to 0.1 optical density) showed no distinct spectral features, only a gently rising background with decreasing wavelength. The solution was examined in an improved magnetic circular dichrometer with a superconducting magnet of 50,000 gauss; the data were evaluated by computer. Detection limits for the system were estimated to be 7 ng/ml for recognition of porphyrin compounds in metal-complexed form. Magnetic circular dichroism spectra of the concentrated extract solution, however, did not show the presence of metalloporphyrins above detection limits.

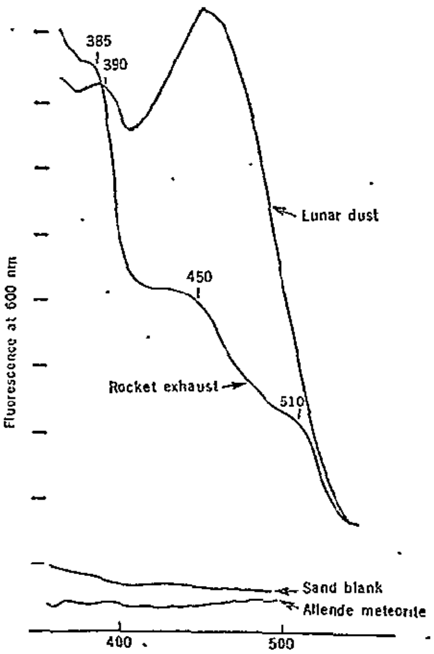


Fig. 1. Fluorescence excitation spectra for extracts of (i) lunar dust from the bulk sample, (ii) dunite exposed to the exhaust of a rocket engine fired at NASA White Sands Test Facility, (iii) crushed Pueblito de Allende carbonaceous chondrite, and (iv) Ottawa sand ignited at 1000°C for 48 hours. Instrument operating parameters were set for highest sensitivity in all cases except that of the rocket exhaust, in which fluorescence was suppressed by a factor of 20.

Free-base porphyrins fluoresce freely, but most metal complexes fluoresce only faintly. Thus, controlled demetallation is useful for the detection of traces of porphyrin metal complexes (*6*). The extract solution was divided into two portions, one four times the volume of the other. Each was reduced to dryness in a spectrofluorometer cell and taken up in 1 ml of diethyl ether. The smaller sample showed a faint excitation band at 410 nm for emission measured at 660 nm upon addition of 2 percent of the demetallating reagent, methanesulfonic acid (MSA). The intensity of the band increased at 7 percent MSA, and at 19 percent MSA the band was replaced by an excitation peak at 388 nm, which became more intense on further addition of MSA.

Recovery of the presumed free-base porphyrins was accomplished by neutralizing the solution with sodium acetate and extracting with ether. The ether layer showed faint excitation bands at 385 and 450 nm. Transfer to 6*N* HCl also showed a weak peak at 390 nm for emission measured at 600 nm, and this peak was interpreted tentatively as a Soret band of porphyrin pigments. To extend the identification of the apparent porphyrin, it was complexed with copper to quench its fluorescence. This was done by transferring the porphyrin to glacial acetic acid and adding cupric sulfate. The excitation band disappeared after a few minutes at room temperature, in accordance with the behavior of authentic porphyrins.

The same analysis was repeated on the other portion of the lunar extract, which corresponded to 10 g of lunar dust. Essentially the same results were obtained, with the emergence of a band at 390 nm for emission at 600 nm on the addition of 20 percent MSA. After demetallation, the fluorescence of the pigments in ether was still weak, but definite emission could be detected at 630 nm for excitation features at 390 and 415 nm. Extraction with 6*N* HCl produced an aqueous layer with emission peaks at 600, 628, and 685 nm. A strong excitation peak was observed at 390 nm, and it appeared to be accompanied by a much weaker peak at 550 nm. The "porphyrins" were transferred back to ether and reextracted with HCl of increasing concentration. The acid strength necessary to transfer the pigments from the organic layer was 4*N* HCl; from this we tentatively concluded that few polar substituents were present to promote the solubility of the pigment in the aqueous phase. Formation of the copper complex resulted in the complete suppression of fluorescence. On the assumption that the pigment was porphyrin, the amount present was estimated to be 1 ng, for a concentration of 10^{-10} g of porphyrin per gram of lunar dust.

The sand blank was examined in the same manner, and it showed no indication of porphyrins above background. In addition, reagents, glassware, and handling procedures were checked for possible contaminants.

A similar demetallation analysis was carried out on the benzene eluate from silica-gel chromatography of the major portion of the benzene-methanol extract of the lunar dust. The hexane and methanol eluates were not available for porphyrin analysis. The benzene eluate left after the completion of other tests appeared to show the presence of a small amount of porphyrin pigments.

Samples of rocket exhaust were made available from the test firing reported by Simoneit *et al.* (7). These comprised samples from trap A, a trap for the exhaust gases cooled to liquid-nitrogen temperatures, and trap E, one containing dunite. Material from trap A showed an intense fluorescence background on which a broad excitation band (in methanol and ether) appeared at 450 nm for emission in the range 600 to 700 nm. In HCl, the exhaust products turned a bright yellow, and an excitation band at 390 nm for emission at 610 nm was clearly present. Absorption spectrometry showed only the yellow color. While the foregoing results suggested porphyrins in the free-base state, MSA demetallation of the total exhaust material—that is, without any chemical fractionation—showed evidence for metal complexes with a 412-nm excitation band appearing at 4 percent MSA. This spectral feature persisted to a concentration of 23 percent MSA; at higher concentrations of MSA a much stronger band emerged at 385 nm and shifted gradually to 392 nm. Attempts to recover free-base porphyrins from the foregoing aqueous acid layers were unsuccessful, however.

Material from trap E gave similar results. Extraction of the sample was carried out in the same manner as that for the lunar sample. A broad excitation band was evident at 450 nm, as in the case of trap A material, but on an intense background. Addition of MSA gave typical demetallation results for metalloporphyrins. At a concentration of 25 percent MSA a strong peak emerged; it increased in intensity with increasing acid content up to 50 percent MSA. Final location of the band was at 387 nm, and the corresponding emission peak was at 595 nm. Magnetic circular dichroism analysis of material extracted from trap E showed a large number of compounds, but none could be definitely identified as porphyrins.

To confirm and extend the previous results and to demonstrate adequate

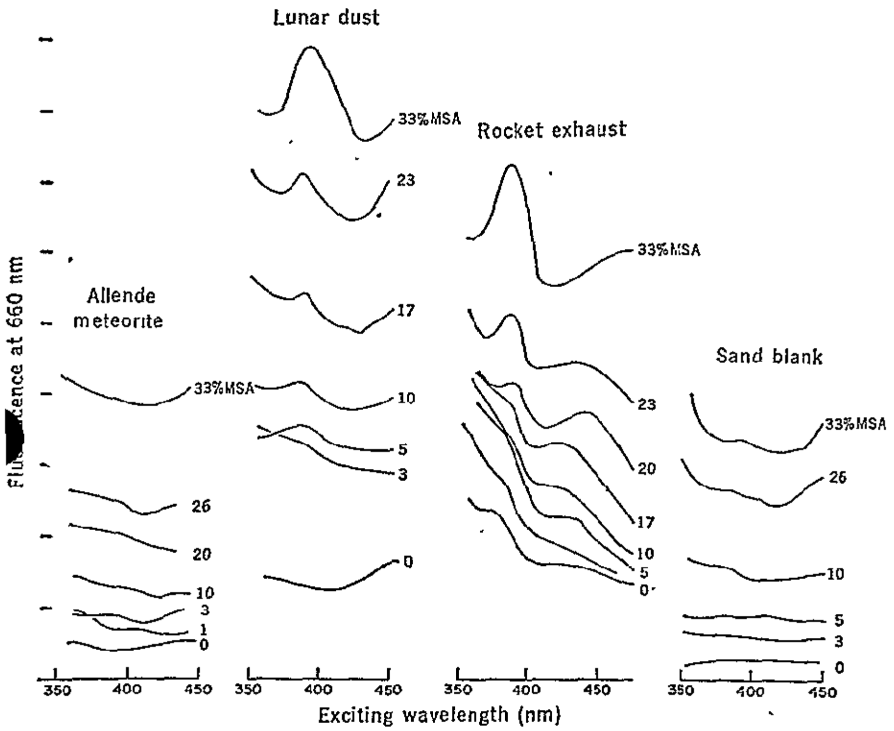


Fig. 2. Demetallation analysis of extracts showing emergence of excitation peaks in the region of the Soret band of porphyrins with increasing content of methanesulfonic acid (MSA). Operating parameters of the instrument were the same in all cases; portions taken for the analyses of lunar dust and rocket exhaust were, respectively, 75 and 11 percent of the total extracts.

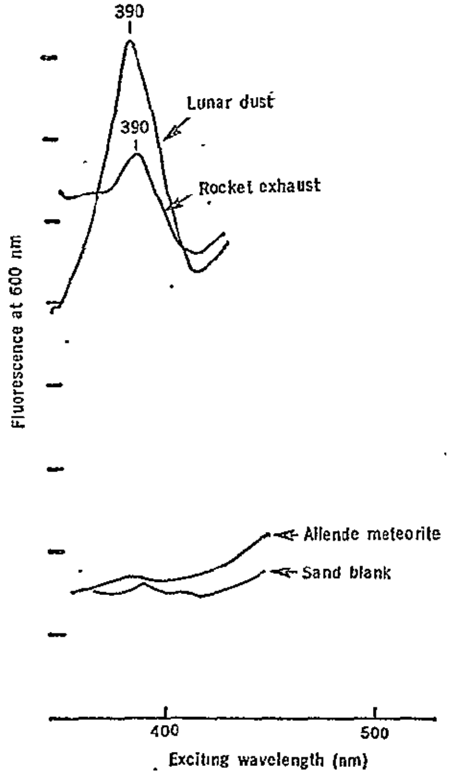


Fig. 3. Fluorescence excitation spectra in Soret region for pigments recovered from MSA demetallation analysis. Operating parameters for spectrofluorometer were the same in all cases. Solvent, 6*N* HCl.

control over laboratory procedures, an additional set of samples was analyzed. Approximately 10 g each of the same lunar dust, trap E dunite, Pueblito de Allende meteorite, and Ottawa sand were extracted with a solution of benzene-methanol (9:1). The extracts were identified by a code unknown to the analysts (G.W.H. and E.P.), and complete analyses were carried out. Figure 1 shows fluorescence excitation curves for the extracts. Demetallation caused by the addition of MSA is illustrated in Fig. 2, and Fig. 3 shows the results of procedures for the recovery of free-base porphyrins. The results from the lunar and exhaust samples confirmed the earlier analyses, and what appear to be free-base porphyrins were recovered from the products of MSA demetallation of both the lunar dust and the rocket exhaust. Results for extracts from both the sand and meteorite were negative.

Organic matter is undoubtedly synthesized extraterrestrially, as indicated for example by the carbonaceous matter of chondrites and the generally accepted graphitic interstellar dust (*8*). Simple compounds containing nitrogen, carbon, hydrogen, and oxygen are reported in interstellar dust clouds (*9*) and in stellar atmospheres (*10*). Recent theories (*11*) postulate that much of interstellar space is occupied by thermally stable gas phases at 10^4 °K, which suggests that high-temperature synthesis of organic matter including porphyrins throughout space is within reason.

GORDON W. HODGSON
University of Calgary,
Calgary 44, Alberta, Canada
ETTA PETERSON
KEITH A. KVENVOLDEN
NASA Ames Research Center,
Moffett Field, California 94035
EDWARD BUNNENBERG
B. HALPERN
Stanford University,
Stanford, California 94305
C. PONNAMPERUMA
NASA Ames Research Center

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4 January 1970

Proceedings of the Apollo 11 Lunar Science Conference, Vol. 2, pp. 1829 to 1844.

Carbon compounds in lunar fines from Mare Tranquillitatis—II. Search for porphyrins

GORDON W. HODGSON
Exobiology Research Group, University of Calgary, Calgary 44, Alberta, Canada

EDWARD BUNNENBERG and BERTHOLD HALPERN
Stanford University, Stanford, California 94305

and

ETTA PETERSON, KEITH A. KVENVOLDEN and CYRIL PONNAMPERUMA
Chemical Evolution Branch, NASA Ames Research Center, Moffett Field, California 94035

(*Received* 28 *January* 1970; *accepted in revised form* 20 *February* 1970)

Abstract—Lunar fines contain porphyrin-like pigments as indicated by fluorescence spectrometry and optical demetallation. Major fluorescence excitation at 390 nm was obtained for 600–690 nm emission. The abundance of porphyrin-like material was estimated to be about $10^{-4}\ \mu g/g$. Similar pigments were found in exhaust products from a lunar descent engine. Although the infall of meteoritic dust to the lunar surface is appreciable and may be expected to contain considerable carbon and associated organic compounds including porphyrins, the data suggest that most if not all of the content of porphyrin-like pigments of the lunar samples was probably introduced during landing of the lunar module. If the pigments in the lunar fines are indeed the product of rocket combustion, a novel synthesis has taken place. Analogous types of syntheses perhaps occur in the cosmos where simple compounds of carbon, hydrogen and nitrogen interact at high temperatures.

INTRODUCTION

PORPHYRINS in meteorites were once regarded as a strong criterion for the existence of extraterrestrial life (BERNAL, 1961), but more recent work has shown that such pigments can arise in experiments simulating prebiotic planetary conditions (HODGSON and PONNAMPERUMA, 1968), and the existence of prophyrins in extraterrestrial samples now has a much broader implication. The appearance of simple organic compounds in interstellar space (SNYDER *et al.*, 1969; CHEUNG *et al.*, 1969), the condensation of graphite from cool stars (DONN *et al.*, 1968) and evidence for molecular absorption of organic compounds in interstellar space (JOHNSON, 1967) suggest that astrochemical synthesis of organic matter of considerable complexity is within reason. The current study based on analysis of lunar fines produced evidence that prophyrin-like pigments were present. These pigments may have been synthesized from unsymmetrical dimethylhydrazine at the temperatures of rocket engines—2000 to 3000°C. Analogous types of syntheses may occur naturally in stellar atmospheres and interstellar space.

This report presents a part of the results obtained by a group of investigators established as the NASA Ames Research Center Consortium to analyse the lunar sample labelled "10086-3 Bulk A fines". Results on the search for porphyrins by the Consortium were recently published in abbreviated form (HODGSON *et al.*, 1970), and the object of this report is to provide more details of the data and to discuss more fully the implications of the findings. Related analyses for porphyrins in lunar dust were

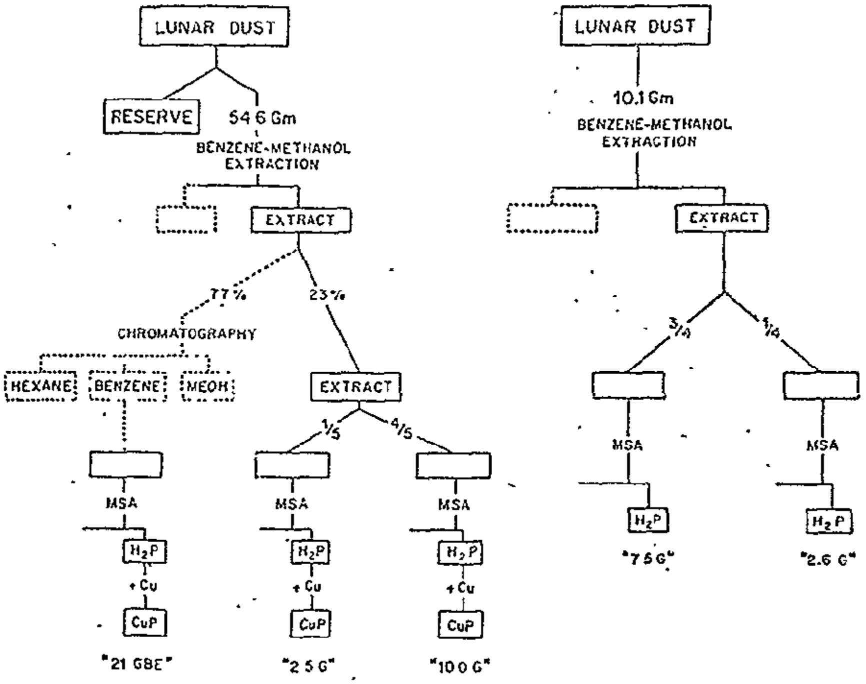

Fig. 1. Left, partial flow sheet for detection of porphyrins in three portions of overall extract obtained for comprehensive organic analysis of lunar sample; right, flow sheet for confirmatory analysis of porphyrins in second sample of lunar fines.

carried out by Rho *et al.* (1970) who used a sequential extraction procedure and gross demetallation by methanesulfonic acid, but no porphyrins were observed.

ANALYTICAL SCHEME

Porphyrins were sought in lunar fines by absorption spectrometry, magnetic circular dichroism (MCD) and fluorescence spectrometry. In addition to passive observations of such spectra, several chemical and physical transformations were carried out on extracts of lunar fines to test the identification of lunar pigments as porphyrins. The analytical approach was briefly outlined by Ponnamperuma *et al.* (1970), and in Part I of this series (Kvenvolden *et al.*, 1970).

A flow sheet relating the analyses for porphyrins to the overall analytical scheme is given in Fig. 1. In the course of examining the lunar samples for porphyrins, five specific portions of lunar extracts were examined as outlined in Table 1. In addition to these, numerous blank runs were made on solvents, reagents and glassware; parallel analyses were done on two sand blanks and on a sample of

Table 1. Description of extracts analysed

Item	Extraction	Portion for porphyrin analysis	Equivalent lunar fines (g)	Sample designation
1	First: 54·6 g	1/5 aliquot of 23% of extract	2·5	2·5 G
2		4/5 aliquot of 23% of extract	10 0	10·0 G
3		1/2 of benzene eluate of 77% of extract	21·0	21 GBE
4	Second: 10·1 g	3/4 aliquot of total extract	7·5	7·5 G
5		1/4 aliquot of total extract	2·6	2·6 G

the Pueblito de Allende carbonaceous chondrite. Similar analyses were performed on substances pertaining to the landing of the lunar module: unsymmetrical dimethylhydrazine, and rocket exhaust products collected in traps A and E described by Simoneit *et al.* (1969). With the exception of some of the control analyses and the MCD measurements, all of the work was done in a "clean" laboratory which was established specifically for analyses of lunar samples.

Absorption and fluorescence spectrometry have been extensively used in previous studies of porphyrins in numerous terrestrial and extraterrestrial samples (Hodgson *et al.*, 1968; Kvenvolden and Hodgson, 1969; Hodgson and Baker, 1969). The fluorescence technique has been especially useful in detecting nanogram concentrations of porphyrins in geochemical substances (Hodgson *et al.*, 1969). The technique involves incremental demetallation of the extracted porphyrin complexes with methanesulfonic acid and the measurement of excitation and emission spectra at each demetallating step. The use of magnetic circular dichroism is novel in its application to the identification of porphyrins. This type of spectrometry was applied to lunar extracts in the hope that confirmation could be obtained for the presence of the porphyrin structure suggested from the fluorescence spectra. Because of this novel application of MCD it will be described in some detail.

Absorption spectrometry

Absorption spectra were obtained directly on lunar extracts using a Cary 14 spectrophotometer with semi-micro cells and a 0–0 1 optical density slidewire.

M[illegible]netic circular dichroism

[illegible]agnetic circular dichroism is a sensitive nondestructive spectroscopic method for the detection of metalloporphyrins, which show three prominent absorption bands in the 350–700 nm region. The positions of these three bands depends on the metal and on the ring substituents. Adopting the nomenclature of Platt (1956), the transition of lowest energy, at about 570 nm, is designated Q_{0-0}; the transition at about 535 nm is a vibrational overtone of the 0–0 band; and the much more intense transition around 400 nm is designated B. The analytically important features in the MCD spectra of metalloporphyrins are the shapes of the MCD bands associated with the Q_{0-0} and B transitions. The effective symmetry of metalloporphyrins is D_{4h} and all bands are degenerate. In a magnetic field the degeneracy is lifted, and one observes the S-shaped MCD bands characteristic of A terms (Buckingham and Stephens, 1966). Previous studies (Stephens *et al.*, 1966) as well as the reference spectra collected for this project (Hodgson and Bunnenberg, unpublished) show that the magnitudes of the A terms of the B and Q_{0-0} bands are comparable even though the absorption coefficients of these bands differ by an order of magnitude. As a representative example, the MCD curve for Mg(II) deuteroporphyrin IX dimethyl ester is shown in Fig. 2. Some metalloporphyrins [e.g. Cu(II) porphine], however, exhibit considerably more intense A terms in the B band than in the Q band. The utility of MCD for detecting small amounts of metalloporphyrins derives from: (1) the intensity of the two prominent MCD bands, (2) their characteristic S-shape, and (3) the observation of two such bands in particular regions of the spectrum. It should be noted that MCD could also be used for the detection of metal-free porphyrins. However, since the MCD bands are much weaker a considerably larger sample would be required.

MCD data were displayed directly in analog form, and in addition were processed by computer in order to gain increased sensitivity. The most secure and conservative sampling mode was used for the lunar sample measurements. The visible portion (335–650 nm) of the spectrum was scanned. The raw data obtained from the lunar sample and the sand blank measurements were corrected for the reference blank (cell plus solvent). The resulting curves were smoothed and are presented in Fig. 3. Measurements were made on a specially constructed MCD instrument (to be described elsewhere) at ambient temperature in a magnetic field of 49,500 G. The light-path length of the cells was 1 cm.

[illegible]ofluorometry and demetallation

Spectrofluorometry was done with an unmodified Turner 210 instrument using standard stoppered 1 × 1 cm cells. For demetallation analysis, the procedures previously described were used (Hodgson *et al.*, 1969).

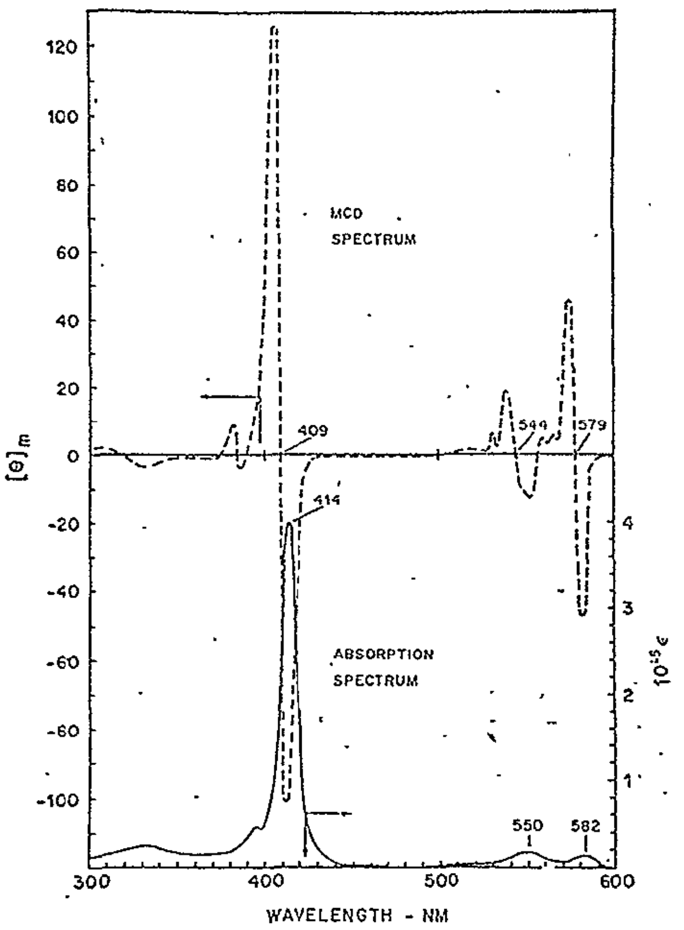

Fig. 2. Magnetic circular dichroism (MCD) and absorption spectra of Mg(II) deuteroporphyrin IX dimethyl ester (7×10^{-5} M) in benzene. A cell of 1-mm light-path was used. The ordinate, $[\theta]_M$, is molar magnetic ellipticity (deg cm^2 G^{-1} decimole^{-1}).

RESULTS

Abundance of specific pigmented compounds in extracts of lunar samples was so low that absorption spectrophotometry failed to reveal any spectral features in the range of porphyrin compounds, i.e. from 350 nm to 700 nm, from which it is concluded that porphyrins, if present, were less than 100 ng per sample. For 10 g samples, the indicated content was less than 10^{-2} μg/g. While magnetic circular dichroism and spectrofluorometry are substantially more sensitive than absorption spectrophotometry, it is clear that any data obtained by the latter methods were not far above their limits of detection, and for that reason were not of customary precision nor entirely free of spectral and chemical noise. In the light of this, a certain subjectivity in treating the data is to be expected, but the major findings are above such questions, with only auxiliary data open to variable interpretation. In some instances, extracts were

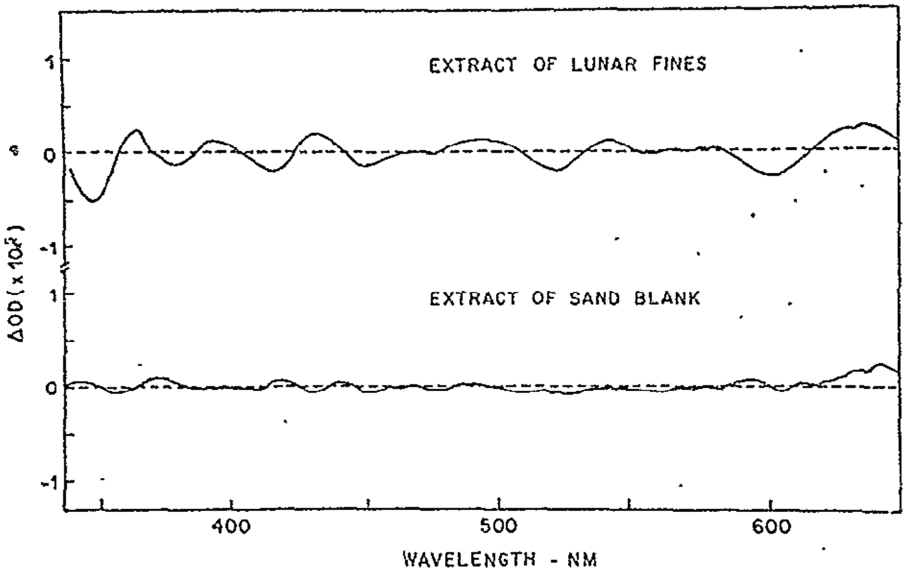

Fig. 3. Plot of magnetic circular dichroism data obtained from lunar and blank extracts as measured in a magnetic field of 49,500 G. The curves have been corrected for the cell plus solvent reference blank. A cell of 1-cm light-path length was used; solvent, methanol.

identified to the analysts only by a code designation, in an attempt to promote complete objectivity.

Absorption spectrophotometry

No evidence of Soret nor non-Soret bands was obtained.

Magnetic circular dichroism

A critical examination of the MCD curve of the lunar extract (in methanol) shown in Fig. 3 reveals that:

1. The *A* term in the vicinity of 570 nm is definitely not present.
2. The approximately equal spacing between the positive and negative signals in the 335–475 nm region strongly suggests that these signals are actually instrumental artifacts, notwithstanding their relatively greater intensities as compared to the MCD curve of the sand blank.

On the basis of the criteria established, we conclude that the amount of metalloporphyrins, if any were present in the lunar extract, must have been less than 7 ng. Thus, examination of the total of samples 2·5 G and 10·0 G before they were divided, i.e. the extract corresponding to 12·5 g of lunar soil, failed to show any spectral responses that could be attributed to porphyrins and their concentration in the lunar [illegible] was therefore less than 6 × 10^{-4} μg/g.

Fluorescence spectrometry

Two extracts of lunar dust corresponding respectively to 12·5- and 10·1-g aliquots of the lunar fines showed considerable fluorescence, as illustrated in Fig. 4. For emission at 625 nm, excitation scans through the Soret region of the spectrum showed a major peak at about 460 nm, with a distinct peak at about 387 nm and a shoulder at about 482 nm. Similar scans were obtained for other emission wavelengths, and in general the practice was adopted of doing multiple excitation "cross scanning" through regions of interest in the emission range, in order to discern more sensitively any emission maxima which on direct observation were badly obscured by background noise. In this manner, families of excitation curves were obtained from which could be established the location of emission maxima.

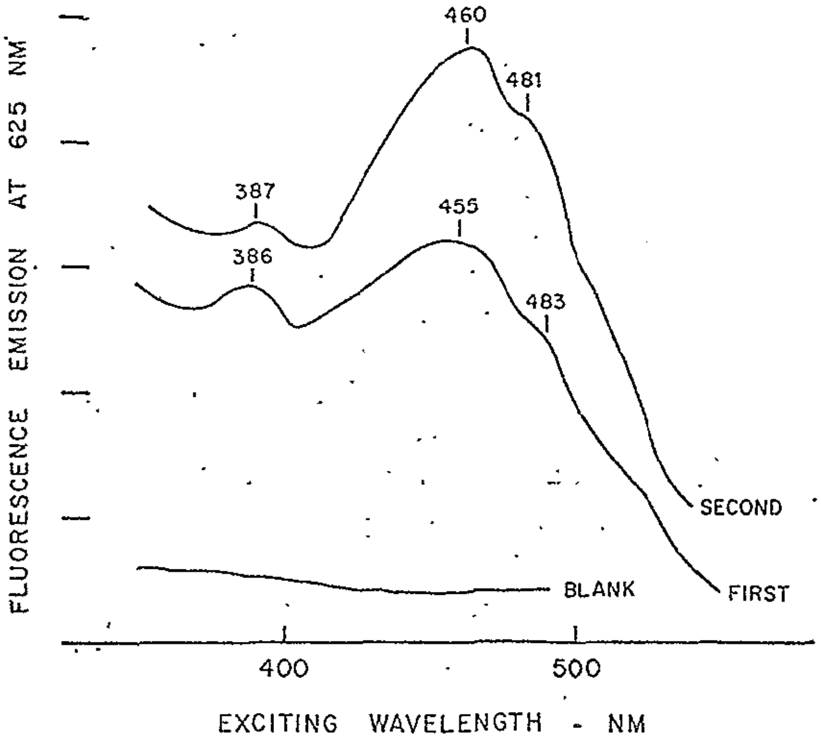

Fig. 4. Excitation spectra of lunar extracts. Solvent, methanol.

Porphyrins do not commonly have Soret absorption above 430 nm, and the excitation features at 460 and 481 nm were not believed to be due to porphyrins. The smaller peaks at 387 nm were tentatively regarded as possible Soret excitations of porphyrins, either free-base or complexed with diamagnetic metals. Complexes with paramagnetic metals were unlikely, since, if present, their Soret bands would have been detected in absorption spectrometry at the levels of fluorescence sensitivity involved.

While information on the chromatographic behavior of the observed pigments would have been helpful, paucity of material precluded such an approach. Some information, however, was available from the examination of solution 21GBE, equivalent to a 21-g sample, which had been chromatographed on silica gel (Part I of this series). Sample 21GBE was the benzene eluate, and it contained some of the same pigments but in substantially lower quantities, from which it is concluded that the pigments of Fig. 4 would have eluted with either n-hexane or methanol. Complexes of porphyrins in terrestrial geochemical samples are generally nickel, vanadyl or iron, and these compounds elute respectively with n-hexane–benzene (9/1 v/v), benzene and methanol (Hodgson *et al.*, 1968).

Analytical demetallation

Methanesulfonic acid was added incrementally to the extracted pigments in diethyl ether with fluorescence monitoring for the onset of demetallating reactions. Figure 5 shows data typical of this approach for the lunar samples. For sample 2·5 G, it shows a short initial period in which no change in fluorescence is noted, after which 2% methanesulfonic acid (MSA) produced a very small excitation feature at 410 nm for emission at 660 nm. This weak band remained unchanged in intensity until about 20% MSA had been added, at which point it was replaced by a much stronger excitation peak emerging at 390 nm. This increased in intensity until 30% MSA was reached, after which it remained nearly constant. Similar behavior was observed for the demetallation of authentic porphyrins of terrestrial rocks (Hodgson *et al.*, 1969) and for porphyrins of carbonaceous chondrites (Hodgson and Baker, 1969). Of particular interest was the observation that the process involved two steps. The

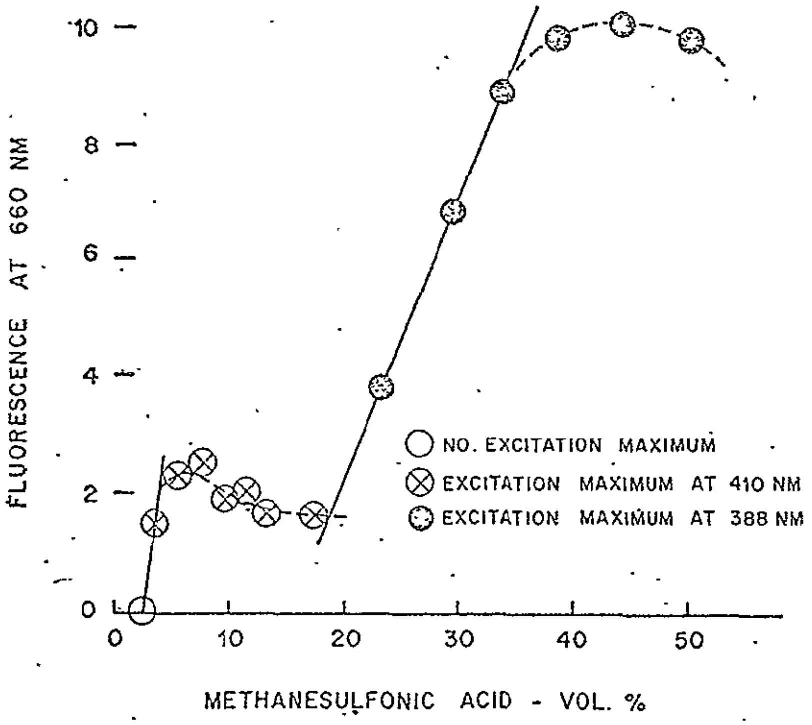

Fig. 5. Demetallation analysis of lunar extract "2·5 G" showing emergence of very weak fluorescence early in the reaction, followed by the major reaction at about 20% MSA.

other four samples listed in Table 1 showed similar demetallation patterns with the same two-stage increase in fluorescence. Summary data for these samples are given in Table 2.

Demetallation at about 25% MSA for the emergence of a Soret band at 388 nm for 660 nm emission is not commonly observed for naturally occurring terrestrial complexes of prophyrins. Threshold values are normally higher, generally in the range above 40% MSA. Soret bands generally appear at longer wavelengths, commonly at 410 nm.

Free-base recovery

The response observed in the course of MSA demetallation analyses was probably due to the generation of free-base porphyrins, and an attempt was made to recover them for further spectral examination and chemical processing. Partition of the products of the MSA treatment between ether and saturated aqueous sodium acetate was used for this purpose.

Table 2. Demetallation of lunar pigments

Sample	Demetallation threshold (%MSA) Initial	Demetallation threshold (%MSA) Major	Soret position (nm) Early	Soret position (nm) Late
2·5 G	2	19	410	388
10·0 G	3	31	410	388
21 GBE	3	25	384	386
7·5 G	5	26	388	387
2·6 G	—	25	(400)	391

Note: "Initial" threshold in all instances was very weak, and estimation of the position of an emerging Soret band was difficult to make.
( ) uncertain.

In the ether layer, excitation attributable to porphyrins was barely discernable. Extraction of the ether layer, however, with 6 N HCl transferred free-base pigments to the aqueous layer where fluorescence was clearly detectable. For example, Fig. 6 shows a family of excitation curves in addition to an emission curve for presumed free-base porphyrins recovered from sample 10·0 G. Emission bands were evident at 600, 630 and 680 nm. Three-band emission spectra are not common for ordinary terrestrial geochemical porphyrins in acid solution, and it remains to be seen whether the observed pigments represent a single class of compounds or a group of two or more with different fluorescent spectra. Terrestrial geochemical porphyrins generally show a single intense emission band at about 660 nm in aqueous acid solution.

Fluorescence characteristics of free-base pigments recovered from the four other samples are shown in Table 3. These data again are different from those for terrestrial geochemical porphyrins in detail, viz. 389 vs. 410 nm for Soret excitation. Porphyrins of carbonaceous chondrites in HCl show a range of positions with a number of samples exciting at 390 nm, closely resembling the pigments of the lunar fines.

Transfer of the lunar pigments to glacial acetic acid for subsequent complexing with copper caused a shift of a few nanometers toward longer wavelengths, as shown in Table 3. This kind of behavior is not unexpected for free-base porphyrins.

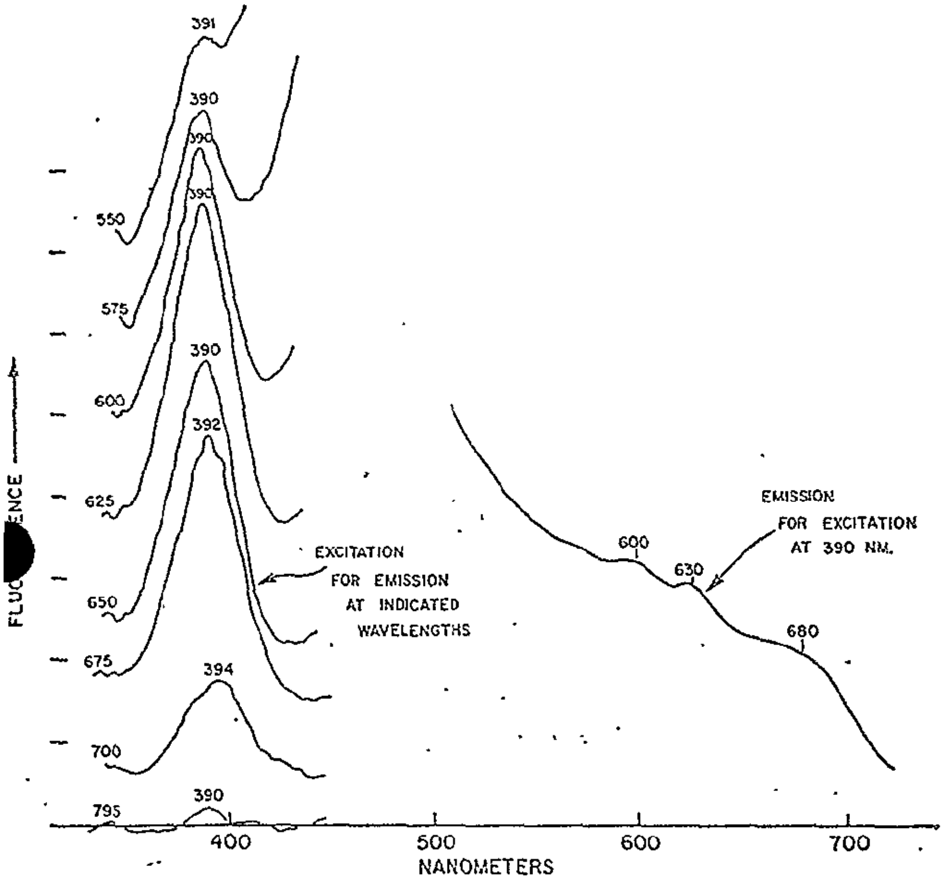

Fig. 6. Emission spectrum of lunar sample "10·0 G" showing fluorescence cross-plotted to confirm relationship between excitation at 390 nm and weak emission bands in the red. Solvent, 6 N HCl.

Table 3. Fluorescence of free-base porphyrins after demetallation

Sample	Solvent		
	Ether	6 N HCl	HOAc
2·5 G	385/660*	389/660	395/660
10 0 G	390/625	390/660 389/630	390/630
21 GBE	388/625 387/690	389/600	392/660
7·5 G	387/625	n/a†	n/a†
2·6 G	n/a	388/620	n/a

* 385/660: Excitation maximum at 385 nm for emission at 660 nm.

† Pigment apparently destroyed by trace of H_2S in HCl solution prepared from HCl gas.

Complexing with copper

To further demonstrate behavior of the lunar pigments consistent with that of authentic porphyrins, the recovered free-base pigments were reacted with cupric acetate in glacial acetic acid to produce non-fluorescing metal complexes. Thus, Fig. 7 shows excitation in the Soret region before the reactions, followed by apparently complete suppression as a result of the complexing reactions.

Abundance

On the assumption that the pigments detected in the demetallation analyses were porphyrins—the spectral data were not consistent with those for azaporphyrins (ELVIDGE, 1956), nor phthalocyanines (MOSER and THOMAS, 1963)—the amount present in the larger samples was estimated to be 1 ng. The smaller samples showed smaller amounts, and the general concentration was therefore indicated to be 10^{-6} μg/g in the lunar fines.

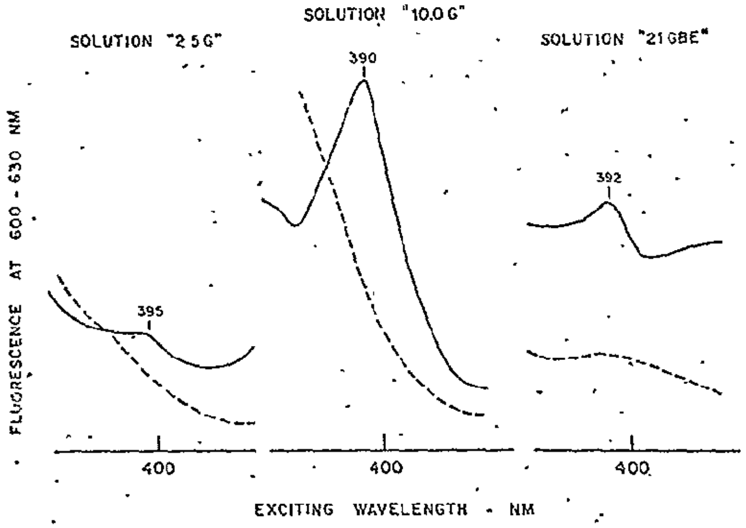

Fig. 7. Fluorescence spectra before (solid lines) and after (dotted lines) complexing with copper, in glacial acetic acid.

Blanks

(i) Solvents and reagents: diethyl ether was purified by distillation; MSA was used as received. Considerable variation was noted, however, in the quality of the MSA as received from the supplier (Eastman #6320) and occasionally freshly-opened bottles could not be used because of the appearance of strong excitation at 380–390 nm in the course of blank runs involving only ether and MSA. In the best blank runs, a small excitation was always observed, and this could not be prevented by ordinary purification procedures involving adsorption or distillation. No evidence of spurious fluorescence was noted for blank analyses involving the other reagents: hydrochloric acid, sodium acetate, cupric acetate and distilled water.

(ii) Complete procedural blanks were run in parallel with analyses of lunar extracts. For lunar samples 2·5 G and 10·0 G a single sand blank was used. It consisted of Ottawa sand fired at 1000°C for 48 hr in the atmosphere. Another aliquot of the same sand blank solution was used with sample 21GBE. A further sand blank prepared in the same manner was used in connection with lunar samples 2·6 G and 7·5 G. Although, as noted above, minor excitation at 380–390 nm was always present in demetallation analyses at high concentrations of MSA, the data obtained for the lunar extracts were always significantly stronger. This is clearly illustrated in Fig. 8 by a direct comparison of the lunar results with those for a sand blank, which shows that the peak height for the lunar extract was more than 12 times greater than that for the blank.

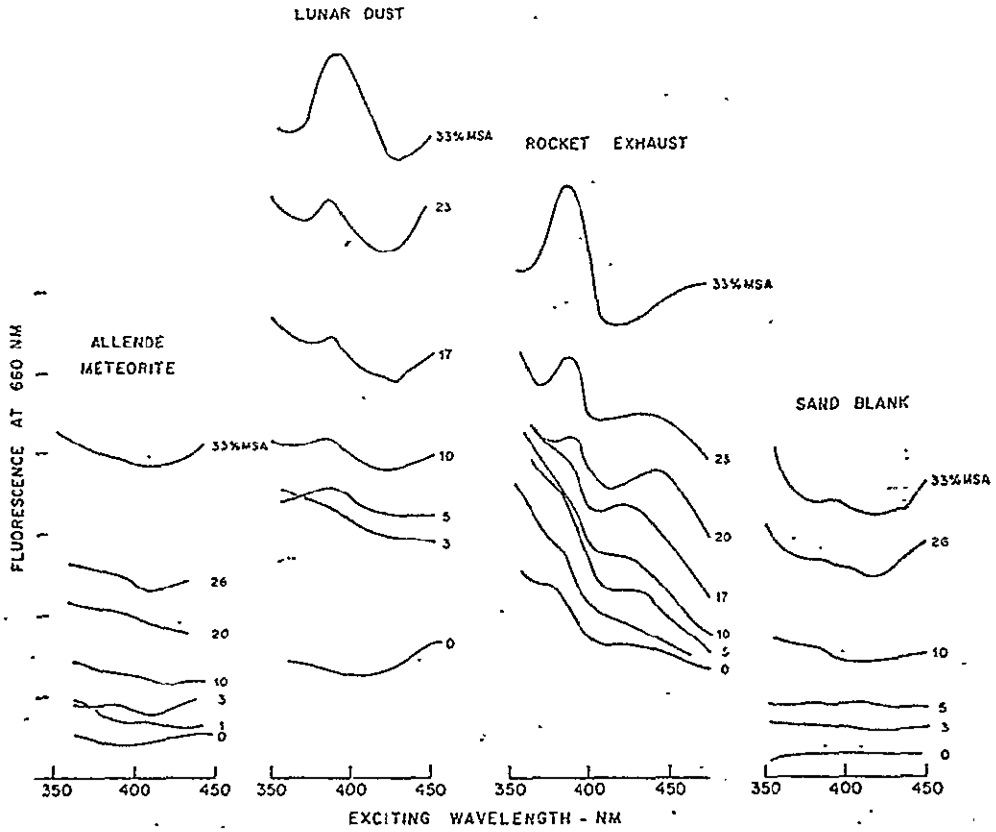

Fig. 8. Comparison of Allende and sand blanks with demetallation analysis for lunar and rocket exhaust determinations.

(iii) Figure 8 also illustrates the difference between the lunar results and those obtained for the demetallation of an extract of a sample of the Pueblito de Allende carbonaceous chondrite included in the same overall analytical program (Part I of this series). Although some samples of this meteorite showed detectable amounts of porphyrins (HODGSON *et al.*, unpublished), the particular sample included in the present study gave demetallation results in which no evidence of the pigments was observed. Thus, the Allende results provided a further check on the control of spurious substances in the course of the analysis for porphyrins.

While the behavior of procedural blanks as outlined above showed that confidence could be placed in the observations obtained for the lunar substances, the 380–390 excitation for emission in the red was unfortunate. The unknown substance which exhibited this fluorescence (which typically amounted to 1–3 per cent of the baseline fluorescence at 33% MSA) did not however, follow porphyrins in subsequent recovery operations for free-base porphyrins and as a result, the likelihood of misinterpretation of demetallation data because of trace impurities in the MSA was very small.

Rocket fuel and exhaust

(i) *Rocket fuel (unsymmetrical dimethylhydrazine).* The lunar descent rocket engine was fueled with unsymmetrical dimethylhydrazine, and while the possibility that this substance contained porphyrins was very slight, it was nevertheless examined for fluorescence responses similar to those observed for the lunar fines. To 1 ml of ether was added 100 μl of unsymmetrical dimethylhydrazine and the customary demetallation analysis carried out. No evidence of porphyrins was obtained, nor was any similarity with the lunar analyses noted.

(ii) *Trap A Exhaust.* A sample of exhaust products from a test firing of a rocket descent engine described by SIMONEIT *et al.* (1969) was obtained from Trap A, through the courtesy of Dr. A. L. Burlingame, University of California, Berkeley. It was collected in the first trap of a series cooled by liquid nitrogen, and contained a wide variety of decomposition and polymerization products involving carbon, nitrogen and hydrogen. As shown earlier (HODGSON *et al.*, 1970), on direct examination by fluorescence spectrometry it exhibited broad excitation at 450 nm and minor excitation at 385 nm, with a shoulder at 510 nm for emission measured at 600 nm. These data are similar to those for the lunar fines illustrated in Fig. 4 measured under essentially the same conditions. Direct extraction of Trap A material with 6 N HCl gave a strong peak at 390 nm; smaller peaks were observed at 470 and 527 nm, as shown in Fig. 9. These results suggest that the compounds tentatively identified in the lunar extracts as porphyrin-like pigments were present in the rocket exhaust to a large degree as free-base porphyrins (or perhaps as metal complexes readily demetallated by 6 N HCl). In addition, the 470 nm peak resembled that of the immediate precursors of porphyrins generated from ammonia, methane and water (HODGSON and PONNAMPERUMA, 1968).

MSA demetallation analysis of Trap A material was obscured by background substances, but initial excitation at 412 nm for emission at 630 nm was detected at 5% MSA. This increased in intensity and persisted until a concentration of about 20% MSA was reached. At approximately 30% MSA the customary 390 nm excitation band appeared and intensified with further additions of MSA. The data obtained on this sample suggest that the pigments detected in extracts of lunar fines were derived directly from the exhaust of the lunar module rocket engine.

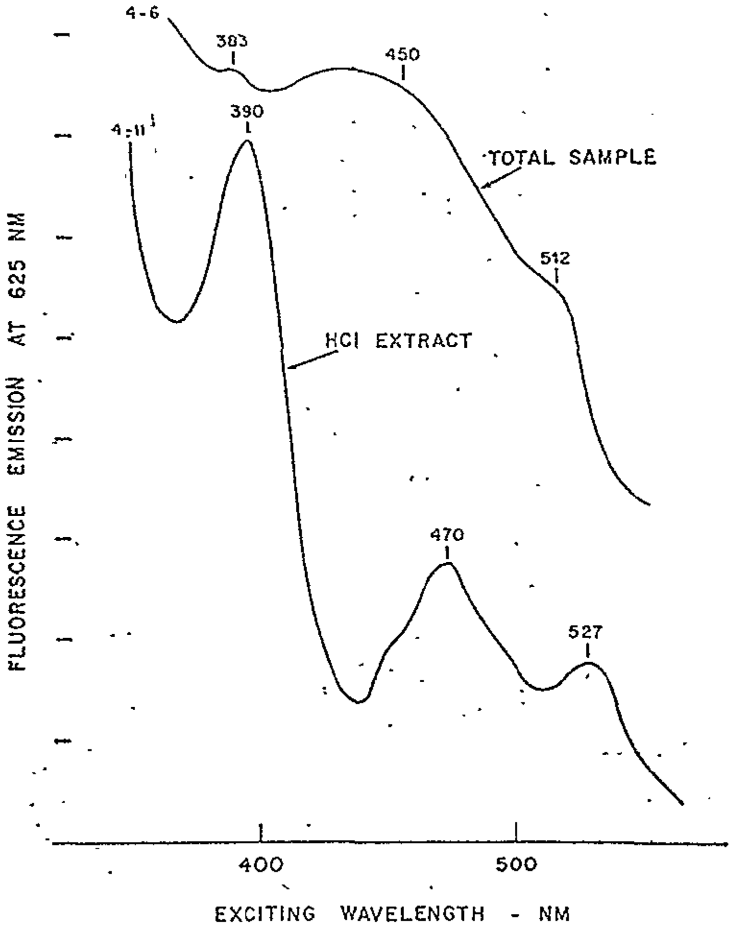

Fig. 9. Fluorescence of trap A rocket exhaust showing evidence for free-base porphyrins in portion soluble in hydrochloric acid.

(iii) *Trap E.* Exhaust products collected in Trap E (Simoneit *et al.*, 1969) supplied by Dr. D. A. Flory, Manned Spacecraft Center, Houston, were extracted from the dunite contained in the trap and treated in the same manner as the lunar fines. Spectrophotometry revealed strong absorption bands at 385 and 365 nm. Figure 10 shows the progress of demetallation analysis after initial examination. It gave essentially the same excitation pattern as for Trap A, as summarized in Table 4. Comparison of the demetallation analysis for this sample with that of a lunar sample is afforded

Table 4. Demetallation of rocket-exhaust pigments

Sample	Demetallation threshold (%MSA) Initial	Major	Early	Soret position (nm) Late	in HCl
Trap A	5	30	412	390	n/a
Trap E	3	29	430	387	388

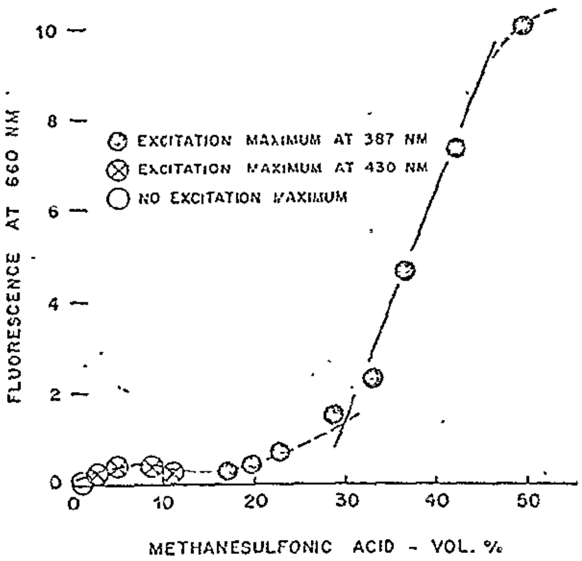

Fig. 10. Analytical demetallation of pigments extracted from trap E.

in Fig. 8 and again, there can be little doubt about the similarity between the behavior of the two samples. The amount of fluorescing pigment in the dunite from Trap E was estimated to be about 50 times that present in the lunar fines.

MCD analyses on rocket exhaust substances failed to confirm the presence of porphyrins. A large number of compounds were indicated to be present, however, and an S-shaped spectral feature was observed at 380 nm. In detail, the band was reversed in sign and rather sharper than is customary for metal complexes of porphyrins. Chromatography on silica gel of rocket products extracted from the Trap E dunite resolved the mixture to some degree with the 380 nm material appearing in the n-hexane eluate. Subsequent eluates (n-hexane–benzene and benzene) were nearly free of this substance and showed much broader bands, but these could not be confidently attributed to porphyrins. Absorption spectrophotometry showed strong absorption at 383 and 361 nm for the hexane eluate, in good agreement with the foregoing data.

CONCLUSIONS

The analytical data collected in the analyses of the lunar fines for porphyrins may be summarized as follows:

1. Fluorescent pigments were present in the lunar fines returned by the crew of Apollo 11.
2. A portion of the pigments appeared to be porphyrin-like.
3. The porphyrin-like pigments of the lunar fines resembled porphyrins detected in carbonaceous chondrites.
4. Rocket exhaust products contained pigments which were similar to those in the lunar fines.

The conclusions to be drawn from the analyses are:

(a) The lunar porphyrin-like pigments were probably derived from exhaust products of the lunar landing module; and

(b) Porphyrin-like pigments appeared to be synthesized from simple compounds containing carbon, nitrogen, hydrogen and oxygen under conditions of very high temperatures.

It is possible that indigenous porphyrins exist on the surface of the moon. These may result from (a) incorporation of carbonaceous primordial matter during the accumulation of the moon (UREY, 1968), and/or (b) the infall of extra-lunar materials during the lifetime of the moon. Little can be evaluated with respect to (a), but (b) can be briefly tested on the basis of indicated infall (KEAYS *et al.*, 1970) and the porphyrin content of carbonaceous chondrites (HODGSON *et al.*, 1969), from which a porphyrin content of about 10^{-5} μg/g of lunar fines is estimated. This is an order of magnitude lower than the measured level, and is therefore in keeping with attributing the bulk of the indicated porphyrins to the combustion products of the rocket.

If a synthesis of porphyrin-like compounds at the temperatures of rocket engines (2000–3000°C) takes place from simple precursors of carbon, nitrogen, hydrogen and oxygen, such a synthesis appears to be a novel process. It is not clear whether the carbon–nitrogen–carbon bond of unsymmetrical dimethylhydrazine remains intact in the process; if it were to do so, it would give rise to a major part of the pyrrole subunits making up the structure of the porphyrins. While the synthesis itself is of interest, it has interesting implications in the context of the generation of moderately complex organic matter wherever simple compounds of carbon, nitrogen, hydrogen and oxygen exist together at very high temperatures. Such conditions may prevail in the cosmos (VARDYA, 1966; FIELD *et al.*, 1969).

NAS9-9439

Acknowledgement—This work was supported by NASA grant ~~NGR-05-020-004~~.

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REPORT ON THE ANALYSIS OF ORGANIC EXTRACTS OF LUNAR SAMPLES H-5 AND CP-10 FROM APOLLO 12 FOR METALLOPORPHYRINS BY MAGNETIC CIRCULAR DICHROISM SPECTROSCOPY

To: B. Halpern and G. W. Hodgson

By: E. Bunnenberg, G. H. Scott, R. A. Stillman, and D. L. Elder
Chemistry Department
Stanford University

and

W. E. Reynolds
Instrumentation Research Laboratory
Genetics Department
Stanford University Medical School

April 27, 1970

REPORT ON THE ANALYSIS OF ORGANIC EXTRACTS OF LUNAR SAMPLES H-5 AND CP-10 FROM APOLLO 12 FOR METALLOPORPHYRINS BY MAGNETIC CIRCULAR DICHROISM SPECTROSCOPY

By E. Bunnenberg, W. E. Reynolds, G. H. Scott, R. A. Stillman,
and D. L. Elder

Abstract: The magnetic circular dichroism spectra of samples H-5 and CP-10 did not provide evidence for the presence of metalloporphyrins. The detection limit, with reference to the Soret band of Mg(II) deuteroporphyrin IX dimethyl ester, is 1 ng/ml.

Introduction

The unique utility of magnetic circular dichroism (MCD) as an analytical spectroscopic technique for the detection of small amounts of metalloporphyrins that may be present in lunar soil can be seen from the MCD spectrum of Mg(II) deuteroporphyrin IX dimethyl ester shown in Figure 1. First, since the molar magnetic ellipticities of the prominent MCD bands have large values, very small amounts of sample are required. Second, the MCD bands have a characteristic and well defined S-shape. Third, the observation of two S-shaped bands in particular regions of the spectrum (around 400 and 580 nm) can be considered to be diagnostic of metalloporphyrins. Finally, the method is nondestructive.

Experimental

The operation of the magnetic circular dichrometer and the data sampling techniques employed were discussed in some detail in the previous report[1] on MCD measurements on extracts from Apollo 11. Consequently, only those experimental details which are pertinent to the Apollo 12 measurements are included in the present report.

Improvements in the magnetic circular dichrometer as well as optimization of the scan conditions with respect to inherent instrument instability have resulted in the establishment of a new detection limit. The detection limit is now 1 ng/ml referred to the Soret band at Mg(II) deuteroporphyrin IX dimethyl ester. Direct plots (i.e., not smoothed) of the MCD curve obtained in the Soret region from a solution containing 1 ng/ml of Mg(II) deuteroporphyrin IX dimethyl ester in 95% ethanol are shown in Figure 2. It should be noted that the diagnostic detection limit is about 3 ng/ml because of the difference in the intensities of S-shaped MCD band in the Soret region and the more prominent one at longer wavelengths.

In order to obtain an optimum balance between the measurement time required for the detection of weak signals under high noise conditions and the inherent instrument long-term instability, the measurement procedure involved separate sample and solvent baseline measurements in the Soret region (350-450 nm) and in the red region (450-650 nm). Since no evidence was obtained from the direct data plots of the MCD curves from either sample in the Soret region measurements were not made in the 450-650 nm region.

Two sampling modes were used for each of the two lunar samples. In the first mode, MPS, the monochromator was stepped from 450 to 350 nm in 0.5 nm steps. At each measurement point 32 cycles of data were taken. In the second mode, RSA, the entire wavelength region (350-450 nm) was scanned repetitively (32 scans for H-5 and 64 scans for CP-10) in 1 nm steps and the data obtained after the repetitive scan cycle was completed were averaged. In each mode the most sensitive scale of the Brower Lock-in-Voltmeter was used (Δ OD = 0.00005 full-scale). The Brower rise-time was 0.1 seconds. The monochromator slit width was 0.5 mm. Separate baselines corresponding to each sampling mode were obtained. The curves discussed in the next section have been corrected for the solvent baseline.

Results

Direct data plots of the MCD curves obtained from sample H-5 are shown in Figures 3a (MPS) and 4a (RSA). The smoothed curves (11 point) are shown in Figures 3b and 4b. Corresponding curves obtained from sample CP-10 are presented in Figures 5 and 6.

Comparison of the MCD curves obtained from samples H-5 and CP-10 with the calibration spectra shown in Figure 2 reveals that metalloporphyrins are not present in the amounts greaater than 1.0 ng/ml.

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Report on the Analysis of an Organic Extract (ARC) of the Lunar Sample for
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E. Bunnenberg and W. E. Reynolds.
October 20, 1969

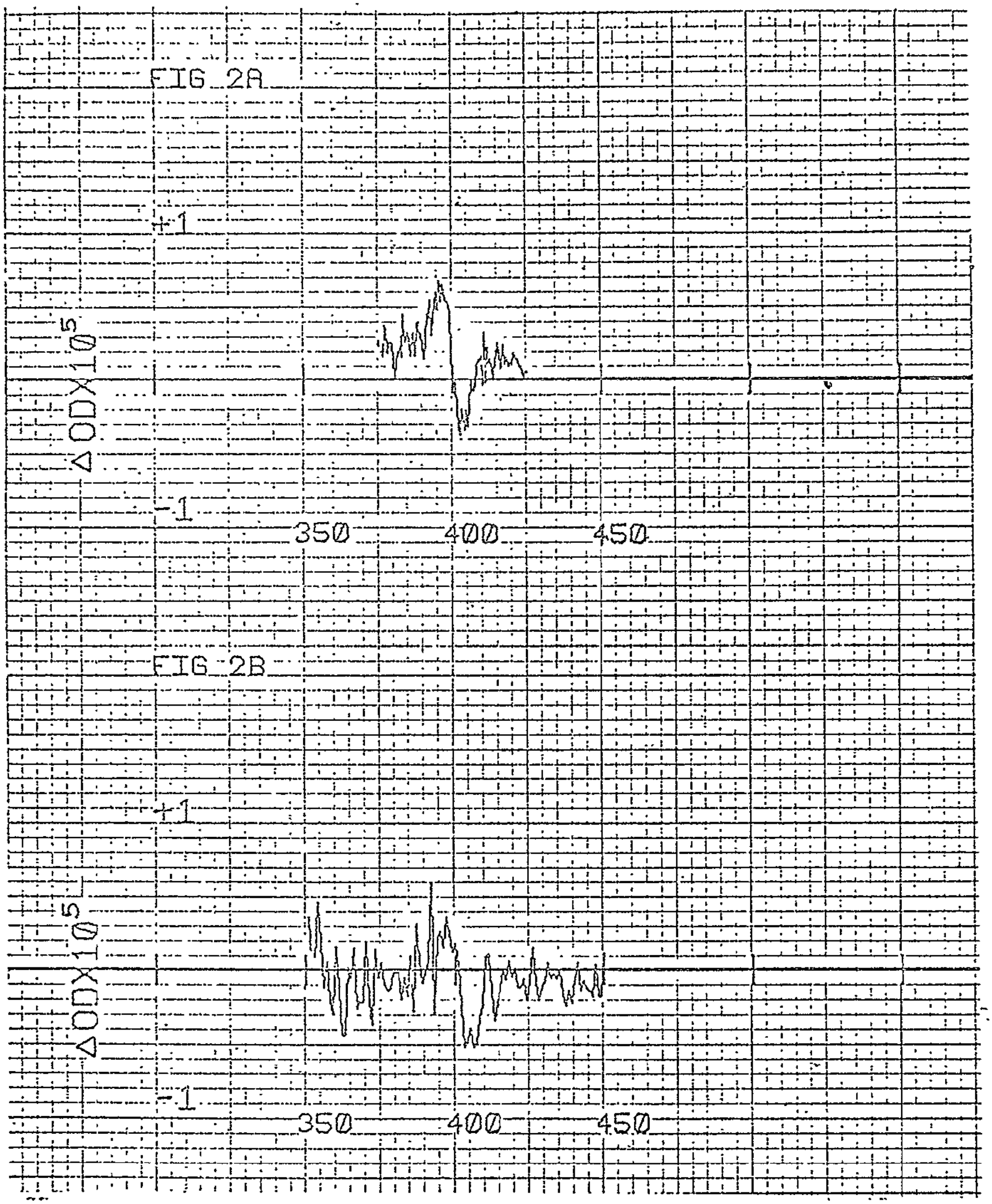

Figure 2. MCD calibration curves obtained from a solution of Mg(II) deuteroporphyrin IX dimethyl ester in 95% ethanol. The concentration was 1 ng/ml and the cell light-path length was 1 cm. In 2a the data was taken in the MPS mode (16 cycles). In 2b the data was taken in the RSA mode (8 scans).

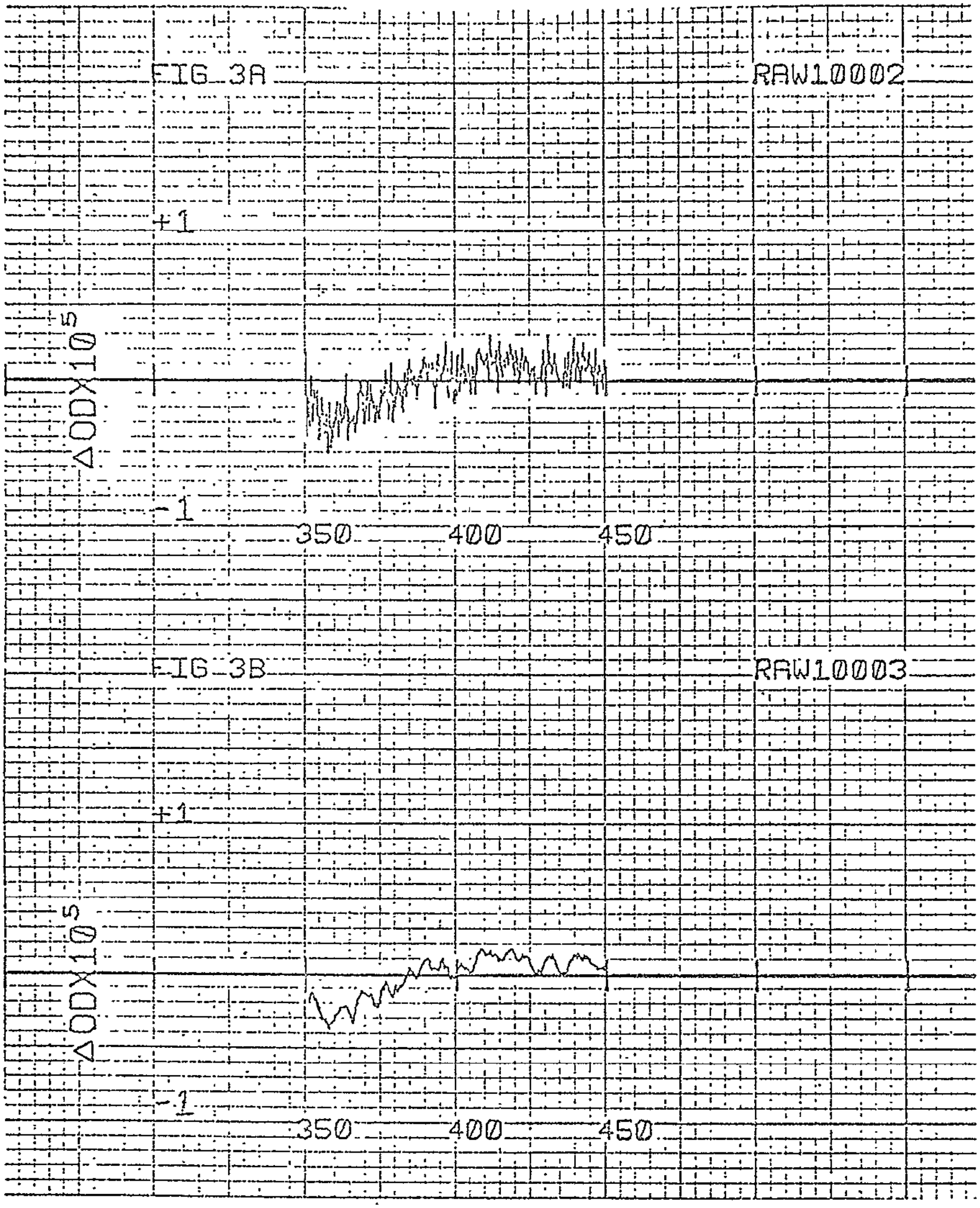

Figure 3. MCD curves obtained from sample H-5 in the MPS mode (32 cycles). The curve in 3a is a direct plot of the data taken whereas the curve in 3b has been subjected to an 11 point smooth.

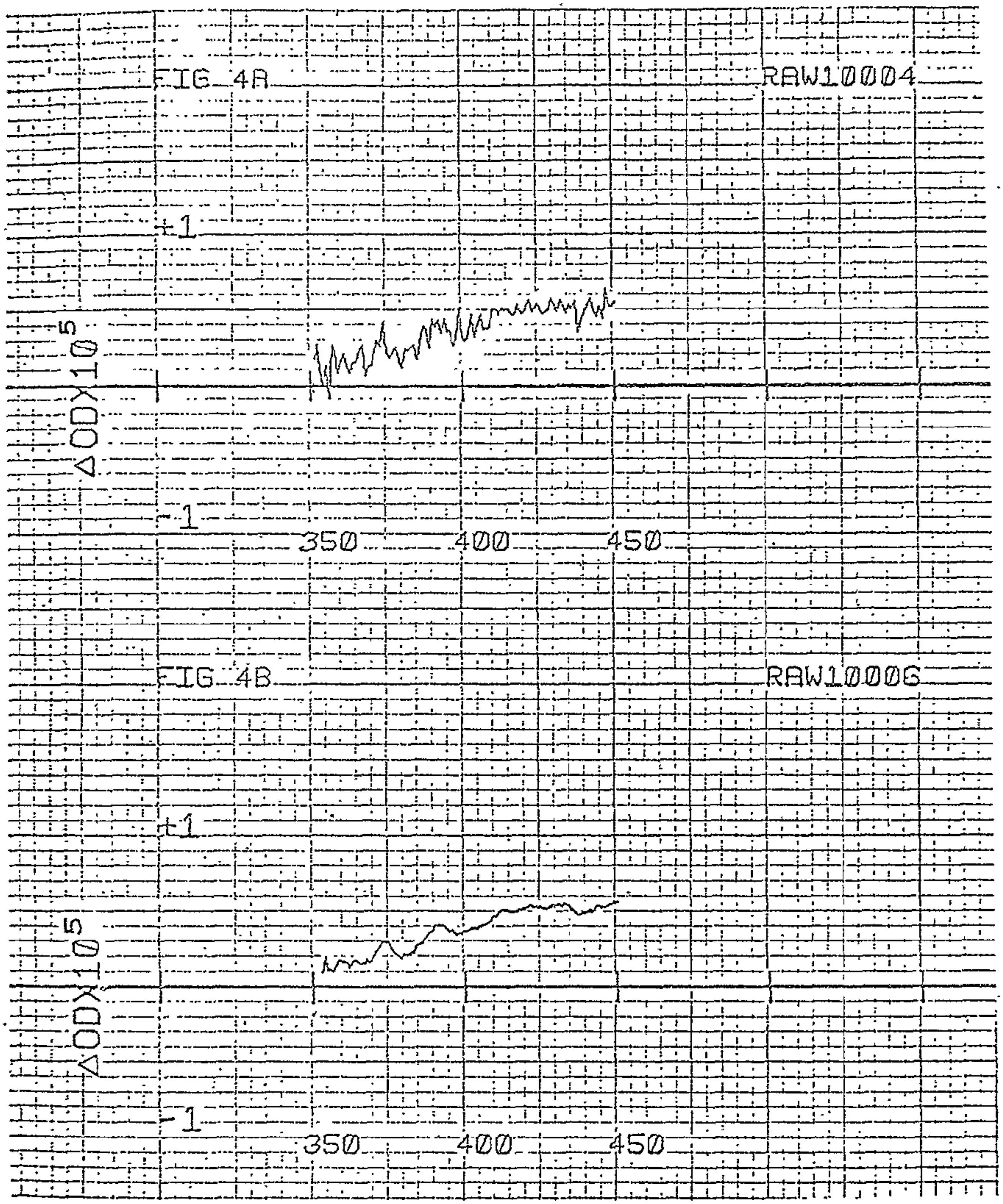

Figure 4. MCD curves obtained from sample. H-5 in the RSA mode (32 scans). The curve in 4a is a direct plot of the data taken whereas the curve in 4b has been subjected to an 11 point smooth.

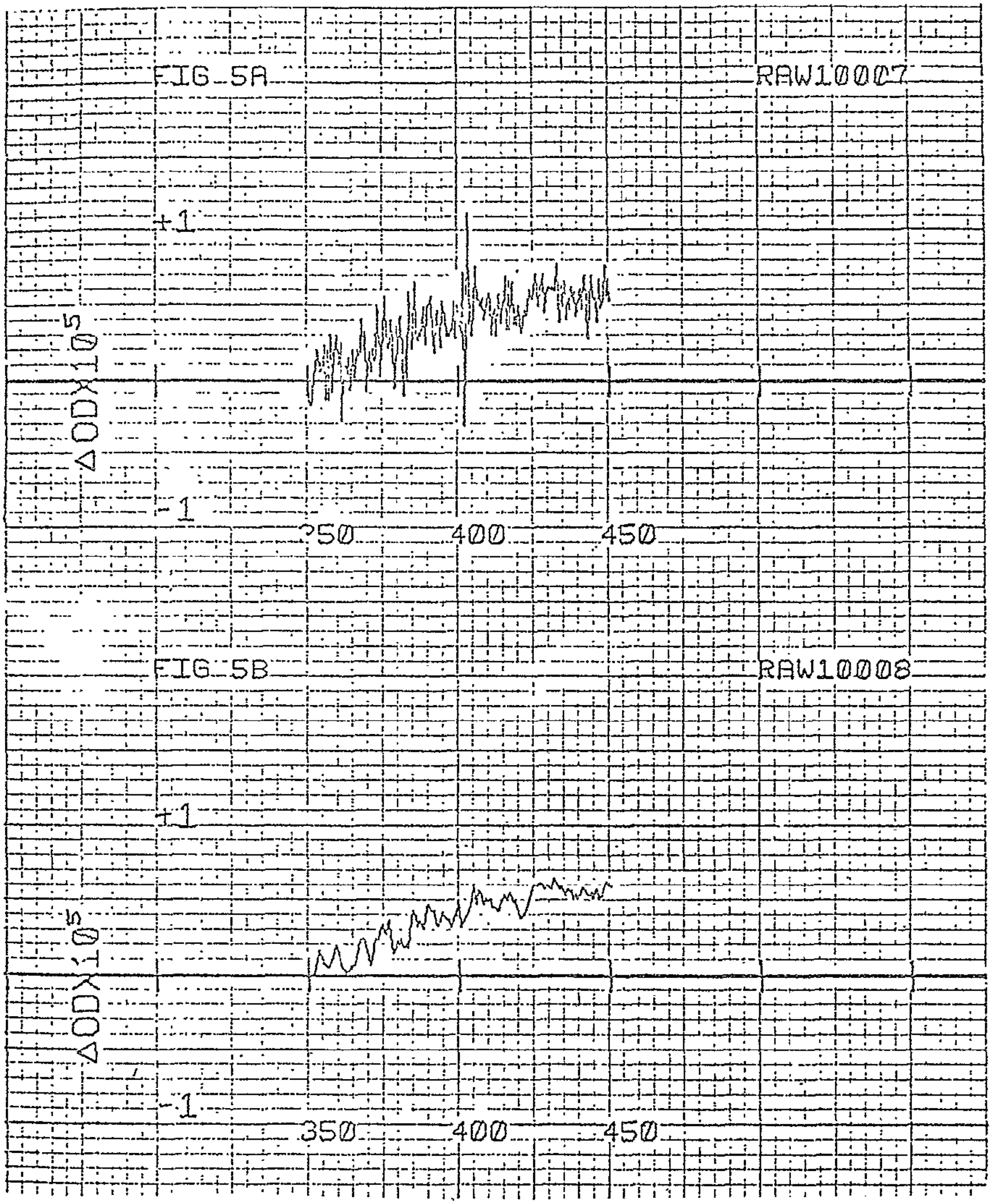

Figure 5. MCD curves obtained from sample CP-10 in the MPS mode (32 cycles). The curve in 5a is a direct plot of the data taken whereas the curve in 5b has been subjected to an 11 point smooth.

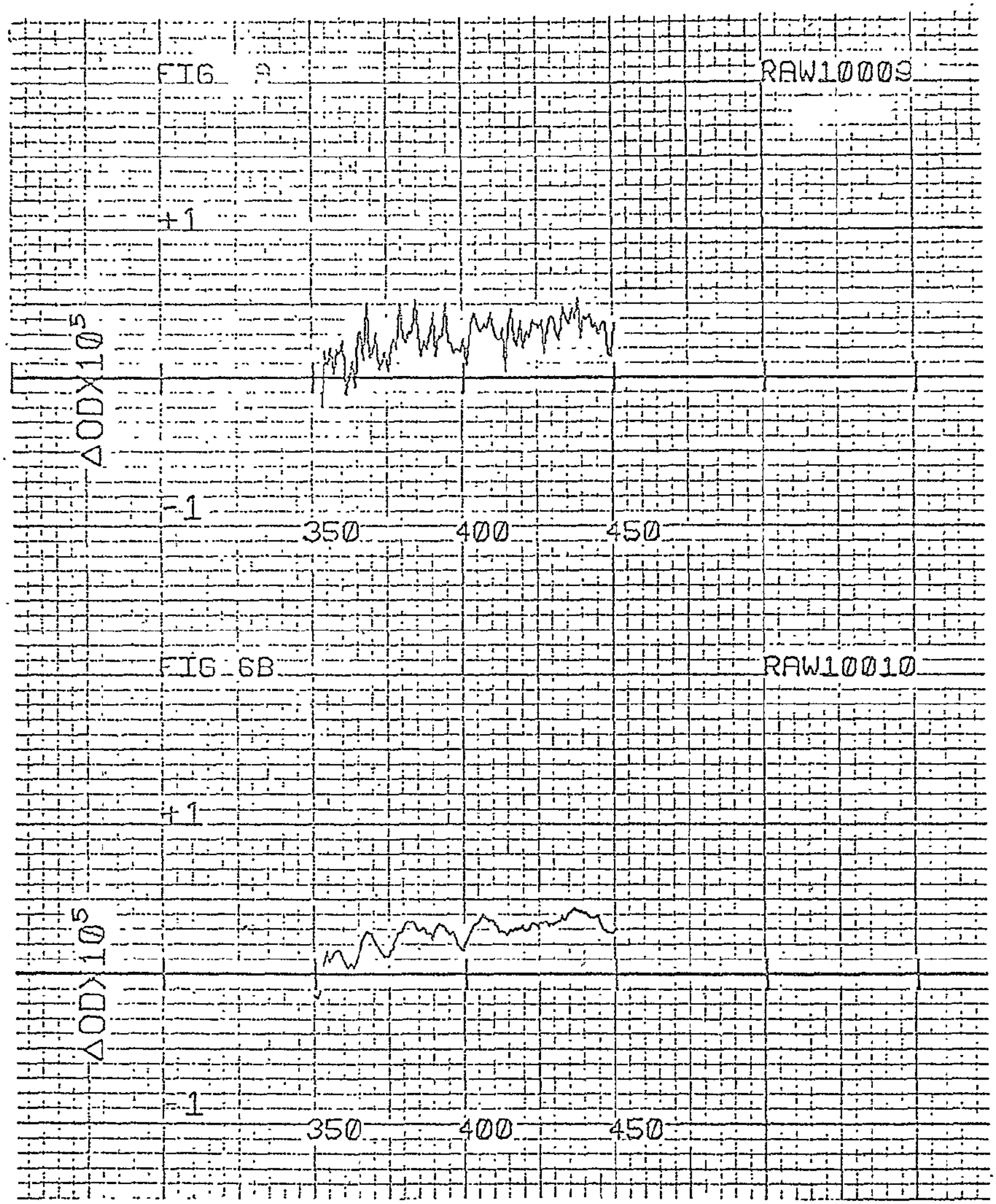

Figure 6. MCD curves obtained from sample CP-10 in the RSA mode (64 scans). The curve in 6a is a direct plot of the data taken whereas the curve in 6b has been subjected to an 11 point smooth.

Lunar pigments: Possible presence of porphyrins in an Apollo 12 sample

by

Gordon W. Hodgson
University of Calgary, Calgary 44, Canada

Edward Bunnenberg and B. Halpern
Stanford University,
Stanford, California 94305

Etta Peterson, Keith A. Kvenvolden and Cyril Ponnamperuma
NASA Ames Research Center,
Moffett Field, California 94035

A manuscript prepared for submission to Science

July 17, 1970

LUNAR PIGMENTS: POSSIBLE PRESENCE OF PORPHYRINS IN AN APOLLO 12 SAMPLE

Abstract. Porphyrin-like pigments were found in a sample of lunar fines (12023) collected on the Apollo 12 mission at a sampling point well removed from the lunar landing vehicle. Abundance of the pigments was estimated to be 5×10^{-5} μg/g. This sample appeared to be free of rocket exhaust products whereas a sample of lunar fines taken from near the lunar module (12001) showed considerable amounts of fluorescent pigments which are attributed to the exhaust of the rocket engine.

The presence of carbonaceous matter and specific organic compounds in meteorites (1), in comets (2) and interstellar space (3) indicates that organic matter is generated extraterrestrially (4). Lunar fines were examined for organic compounds (5), and evidence was obtained for the presence of porphyrins in the fines of the Sea of Tranquillity (6). These pigments were thought, however, to be due in part at least to a novel synthesis of porphyrin-like compounds from unsymmetrical dimethylhydrazine taking place in the firing of the retro-rocket of the lunar module (LEM). In that investigation the question of whether porphyrins were indigenous to the lunar surface was not answered. The present study afforded a further opportunity to attempt to resolve the question through the availability of two samples of lunar fines from widely spaced locations visited during the extravehicular activity of the Apollo 12 mission. One sample (12001,27) was collected near the LEM, and was designated as the <u>close-in</u> sample; the other was taken at a location most remote from the landing point, 440 m from the LEM and 500 m from the site of Surveyor 3 (7).

It was a portion of sample 12023 which had been packaged in the lunar environment sample container (LESC). This sample was taken from a trench 20 cm below the lunar surface. It was designated as the remote sample. Thus the likelihood of contamination from the retro-rocket was high in the case of the close-in sample and low for the remote sample. The close-in sample exhibited fluorescent pigments characteristic of rocket exhaust similar to the findings in Apollo 11; the remote sample was free of such contaminants and showed the presence of porphyrin-like compounds.

The methods used in the present study were substantially the same as those used in the Apollo 11 search for porphyrins (6). The overall organization of the analysis of the lunar samples was the same as before. The samples used are listed in Table 1 along with the blank samples included in the study: Pueblito de Allende meteorite, basalt lava from Hawaii and tektite from Thailand. The lunar samples were extracted directly in the benzene-methanol (9:1) and the organic extracts were subjected to spectral analysis involving fluorescence, absorption and magnetic circular dichroism (MCD) spectrometry. This was followed with analytical demetallation for porphyrins (8), after which free-base recovery and remetallation procedures were undertaken. Improvements in the methods centered on a sharp increase in sensitivity for the MCD examination, and on more extensive remetallation of the free-base pigments. Attempts were also made to determine if any fluorescent organic pigments were imbedded within the mineral grains of the lunar soil.

Blank analyses involving solvents and reagents were consistently negative. Sample sizes for the blank determinations ranged from 5 to 10 g, and results for all of these were below detection limits. Detection limits for porphyrins were re-determined from those reported earlier (8) by using deuteroporphyrin dimethyl ester in free-base form in 6 N HCl in such a manner that the results would apply directly to the lunar analysis samples. Excitation spectral responses were clearly discernable above background noise for 0.05 ng of free-base porphyrins, and considering all of the analytical factors involved in analyses of lunar samples the detection limits for such samples were taken to be 0.1 ± 0.05 ng. Work with the authentic porphyrin was done after all of the lunar and blank analyses had been completed to avoid possible contamination of the analytical system. Detection limits were determined for the improved MCD method using the magnesium complex of deuteroporphyrin under the same conditions as were used for the analysis of the lunar extracts. The MCD detection limit for metalloporphyrins was taken to be 3 ng.

Direct spectrofluorometry of the extract from the sample of lunar fines taken from near the LEM showed nearly the same type of response as that for the Apollo 11 samples, namely a strong broad excitation band at 450 nm for emission at 660 nm (6). Partitioning between ether and hydrochloric acid resulted in all of the fluorescing pigments remaining in the organic phase and accordingly there was no indication of free-base porphyrins at this stage. A weak excitation band observed at about 390 nm in the Apollo 11 analyses was not clearly detected in the present determination. Neither absorption nor MCD spectrometry showed the presence of porphyrins. The 450/660 nm fluorescence was probably due to rocket exhaust as suggested in the Apollo 11 analyses (6).

Methanesulfonic acid (MSA) was used to demetallate any porphyrin complexes present in the extract of the <u>close-in</u> sample. Porphyrins did not appear above the background fluorescence, in contrast to the results for Apollo 11 in which porphyrin-like pigments were observed to demetallate at this stage with a threshold of about 25% MSA in ether. Regular recovery procedures were used to search for free-base pigments in the products of the MSA reaction, but little if any indication of such pigments was obtained.

Direct spectrofluorometry of the organic matter extracted from the <u>remote</u> sample showed no discernable excitation in the region from 350 to 500 nm for emission in the red end of the visible spectrum. There was no indication of free-base porphyrins, nor of fluorescing pigments associated with rocket exhaust. Figure 1 shows the marked difference between the extracts of this sample and those of the sample taken from near the lunar module. Absorption spectrophotometry showed nothing. MCD spectrometry, after data aquisition and reduction by computer, did not show bands that could be attributed to metal complexes of porphyrins.

The extraordinary low background of fluorescence in the extract of the <u>remote</u> sample made it possible to detect the onset of a weak excitation band in the MSA demetallation analysis. This band emerged at about 420-425 nm for emission in the 600-700 nm range. The threshold for the reaction was about 50% MSA and the intensity of the band increased moderately during the latter part of the analysis. Recovery of presumed free-base pigments was accomplished in the usual manner after the concentration of MSA reached 70%. Free-base recovery showed no specific fluorescence in ether solution probably because of extensive quenching commonly observed

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during this stage of the analysis. Extraction of the ether solution with 6 N HCl revealed a fluorescent pigment exciting at 390 nm for emission in the customary porphyrin range. Cross-plotting of the excitation data to reduce the effect of background fluorescence showed emission maxima at 590 nm (minor band) and 623 nm (major band) as illustrated in Figure 2. Authentic porphyrins commonly show double-banded emission in the red end of the spectrum in HCl solution, e.g., deuteroporphyrin dimethyl ester, at 606 and 660 nm. Comparison of similarly plotted excitation data for the porphyrin-like compounds of the Apollo 11 samples showed maxima at 625 and 680 nm and for this reason were clearly distinguishable from those of the <u>remote</u> sample of Apollo 12. On the assumption that the Apollo 12 pigments were porphyrins, their abundance was estimated to be 0.5 ng, corresponding to 5×10^{-5} μg/g. The amount detected was about 5 times above the detection limit of the method.

The pigments recovered from the <u>remote</u> sample were subjected to remetallation procedures (contact with metal acetates in glacial acetic acid at 100°C for about 10 min.) involving copper and zinc to give non-fluorescing and fluorescing complexes respectively, after the manner of authentic porphyrins. Although the amounts of presumed free-base porphyrins available for the test were very small, major quenching was observed for the copper complex, and minor quenching for the zinc complex.

Table 2 summarizes the several fluorescent pigments encountered in the search for porphyrins in lunar samples and related samples from the Apollo 11 and 12 missions. Four classes of pigments were detected: "A", "B", "C" and "D". Pigment "A" comprised organic substances fluorescing at 450/600 nm (450 nm excitation for 600 nm emission). They were present in <u>close-in</u> Apollo

11 fines and rocket exhaust, and also in the <u>close-in</u> sample of Apollo 12. These compounds were not porphyrinic. The other three groups of pigments resembled porphyrins. "B" behaved like a free-base porphyrin, and "C" was probably the same pigment complexed with metals. Both were present in the several samples analysed from the Apollo 11 mission. Pigment "D" appeared also to be a metal complex of a porphyrin, but it was distinguishable from "C" since (1) the MSA demetallation threshold was 50% contrasted with 25% for "C", and (2) that the pairs of emission bands were not only different in position but different in relative intensity.

Whether the porphyrin-like pigments are surficial or imbedded has implications with regard to the origin of the material. The <u>close-in</u> sample was exhaustively extracted in the as-received state and then re-extracted after crushing the mineral grains in a mortar and pestle. In addition, the fines were etched with hydrofluoric acid. Neither approach appeared to release additional pigments. Crushing of the <u>remote</u> sample also failed to release more fluorescent pigments. It is concluded that all of the fluorescent pigments are either on the surface of the mineral grains or exist in porous particles readily penetrated by organic solvents. The results suggest that the porphyrin-like pigments "D" may have come from extralunar particles with physical structures similar to types I and II carbonaceous chondrites. At least 1% of the lunar regolith is believed to be due to the infall of extralunar materials resembling carbonaceous meteorites (9).

GORDON W. HODGSON

University of Calgary,
Calgary 44, Alberta, Canada

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EDWARD BUNNENBERG,
B. HALPERN

Stanford University,
Stanford, California 94305

ETTA PETERSON,
KEITH A. KVENVOLDEN,
CYRIL PONNAMPERUMA

NASA Ames Research Center,
Moffett Field, California 94035

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10. This work was supported by NASA grant NAS 9-9439.

TABLE 1

SAMPLES ANALYZED

No.	Description	Identification	Wt. Analyzed, g.
1.	Lunar, Apollo 12 - close-in to lunar module	12001,27	5.0147
2.	Lunar, Apollo 12 - remote from lunar module	ARC 12023.03	10.111
3.	Pueblito de Allende - interior of large individual (Kvenvolden et al., ref. 5)	NASA 31-4A	10.00
4.	Basalt - Kilauea eruption, Hawaii, Aloi-Alae, February, 1970	NASA 040270	10.40
5.	Tektite - N.E. Thailand	NASA 040770	5.05

TABLE 2

Summary of Presence of Fluorescent Pigments in Lunar Samples from Apollo 11* and 12 and Related Blanks

		Fluorescent Pigments			
		"A"	"B"	"C"	"D"
Excitation/emission		450/600 nm	390/600 nm	390/625 nm	390/625 nm
Demetallation threshold		0% MSA	0% MSA	25% MSA	50% MSA
Pigment characteristics		not porphyrin	porphyrin-like	porphyrin-like	porphyrin-like
Solvent partition test		organic	free-base	complexed	complexed
Apollo 11	10,086 (i) fines	PRESENT**	PRESENT	PRESENT	P/M
	(ii) fines	PRESENT	PRESENT	PRESENT	P/M
Apollo 11	Trap A, exhaust	PRESENT	PRESENT	PRESENT	P/M
	Trap E, exhaust	PRESENT	PRESENT	PRESENT	P/M
Apollo 12	Basalt blank	BDL	BDL	BDL	BDL
Apollo 12	Lunar dust, close-in	PRESENT	DL	DL	P/M
Apollo 12	Tektite blank	BDL	BDL	BDL	BDL
Apollo 12	Lunar dust, remote	BDL	BDL	BDL	PRESENT
Apollo 12	Allende blank	BDL	BDL	BDL	BDL

---

* Apollo 11 data summarized from reference (6).

** Notes:

"PRESENT"	- pigment is present at levels significantly above detection limits.
P/M	- pigment may be present but masked by other pigments.
BDL	- below detection limits.
DL	- pigment possibly present, but only near detection levels -- detection very uncertain.

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FIGURE CAPTIONS

Figure 1. Direct fluorescence examination of extracts of two samples of lunar soil from the Apollo 12 mission. Included also are corresponding data for a procedural blank. Note that fluorescing pigments evidently from rocket exhaust are not present in the remote sample.

Figure 2. Cross-plotted data for apparent free-base porphyrins recovered from demetallation analysis of remote sample of lunar soil. Removal of background fluorescence reveals clear-cut minor band (590 nm) and major band (625 nm). Curve for porphyrin-like pigments of Apollo 11 samples was constructed from data previously given in figure 6 of ref. 6; that for deuteroporphyrin from direct emission for 400 nm excitation. 6 N HCl solvent in all cases.

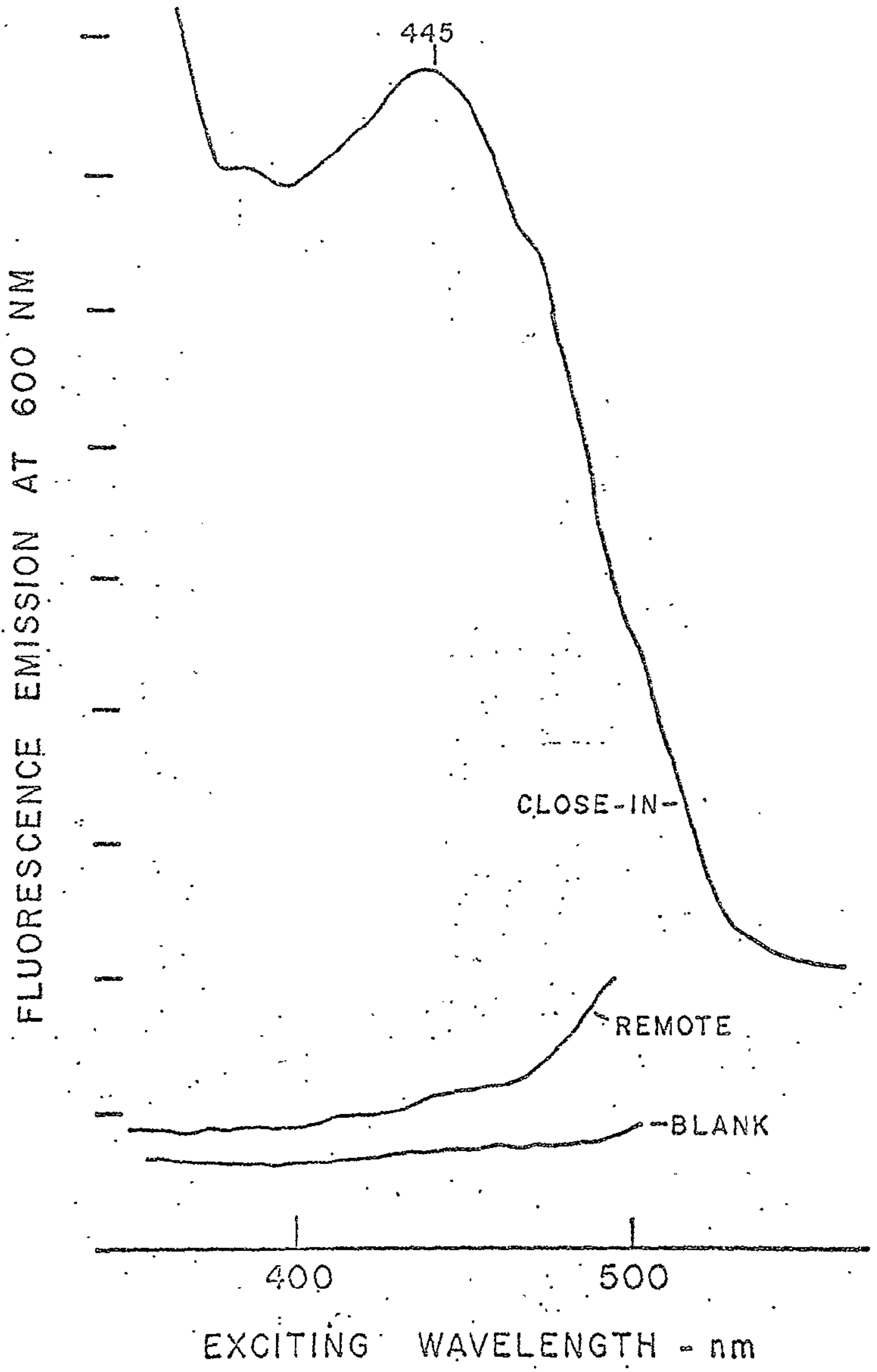

Fig. 1

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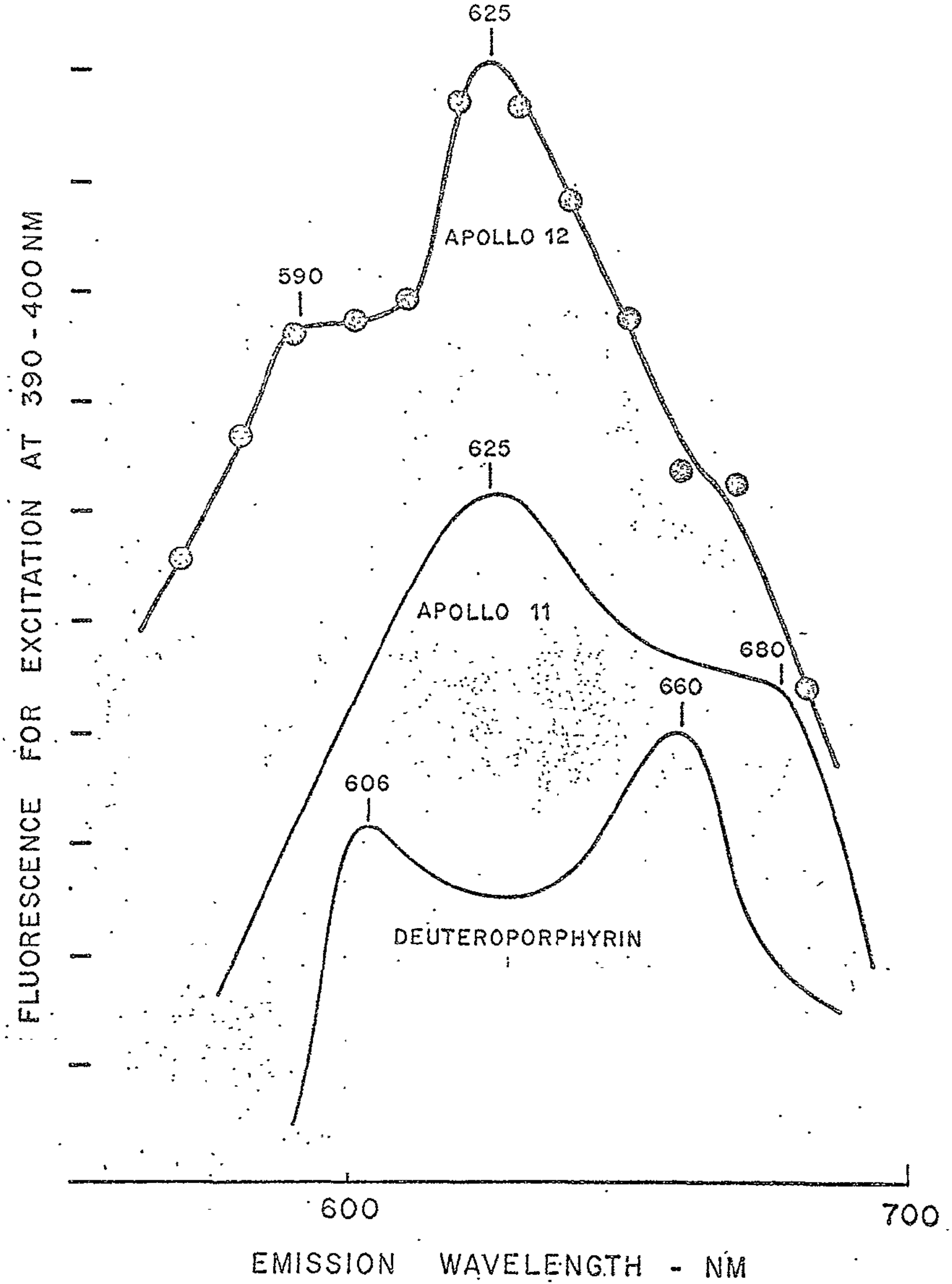

Fig. 2

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REPORT ON THE ANALYSIS OF AN ORGANIC EXTRACT (ARC) OF THE LUNAR SAMPLE FOR METALLOPORPHYRINS BY MAGNETIC CIRCULAR DICHROISM

by E. Bunnenberg and W. E. Reynolds

Abstract

The magnetic circular dichroism spectra of sample ARC did not provide evidence for the presence of metalloporphyrins. The detection limit, with reference to Mg(II) deuteroporphyrin IX dimethyl ester, is about 7 ng/ml.

Introduction

The purpose of this investigation has been to provide a sensitive nondestructive spectroscopic method, magnetic circular dichroism (MCD), for the detection of metalloporphyrins in lunar extracts. MCD is a particularly useful technique for this purpose since the observation of two S-shaped bands in the MCD spectrum of the lunar extract would provide more secure evidence for the presence of these compounds than is available from other spectroscopic techniques. A very brief discussion of the electronic transitions and MCD spectra of metalloporphyrins will indicate the analytical application of this method.

Metalloporphyrins show three prominent absorption bands in the 350-700 nm region. The positions of these three bands depends on the metal and on the ring substituents.[1] Adopting the nomenclature of Platt[2], the transition of lowest energy, at about 570 nm, is designated Q_{0-0}; the transition, Q_{0-1}, at about 535 nm is a vibrational overtone of the 0-0 band; and the much more intense transition around 400 nm is designated B. The analytically important features in the MCD spectra of metalloporphyrins are the shapes of the MCD bands associated with the Q_{0-0} and B transitions. The effective symmetry of metalloporphyrins is D_{4h} and all bands are degenerate. In a magnetic field the degeneracy is lifted, and one observes the S-shaped MCD bands characteristic of A terms.[3] The A terms associated with the Q_{0-0} and B bands are indicated in the MCD spectrum of Mg(II) deuteroporphyrins IX dimethyl ester shown in Figure 1. Previous studies[4] as well as the reference spectra collected for this project[5] show that the magnitudes of the A terms of the B and Q_{0-0} bands are comparable even though the absorption coefficients of these bands differ by an order of magnitude. The MCD curve for Mg(II) deuteroporphyrin IX dimethyl ester was recorded under the experimental conditions used for the lunar sample measurement. Under conditions suitable for larger samples the magnitudes of the A terms are more nearly comparable (see experimental section). Some metalloporphyrins (e.g., Cu(II) porphine), however, exhibit considerably more intense A terms in the B band than in the Q band. The utility of MCD for detecting small amounts of metalloporphyrins derives from: (1) the intensity of the two prominent MCD bands, (2) their characteristic S-shape, and (3) the observation of two such bands in particular regions of the spectrum.

Figure 1. Magnetic circular dichroism spectrum of Mg(II) deuteroporphyrin IX dimethyl ester in 95% ethanol recorded under the conditions used for measurement of the lunar sample ARC. (c = 2.24 micrograms/ml, l = 1 cm)

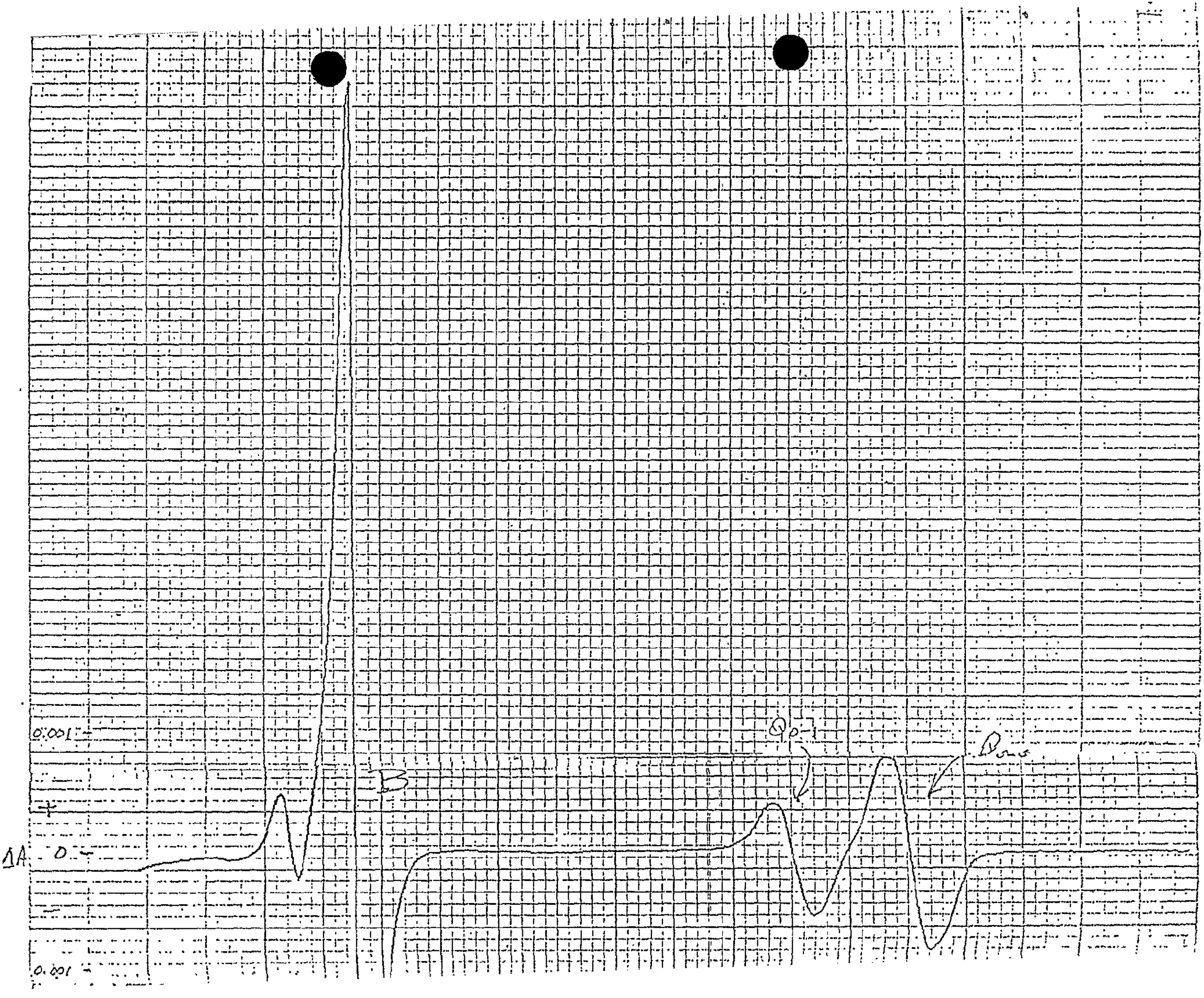
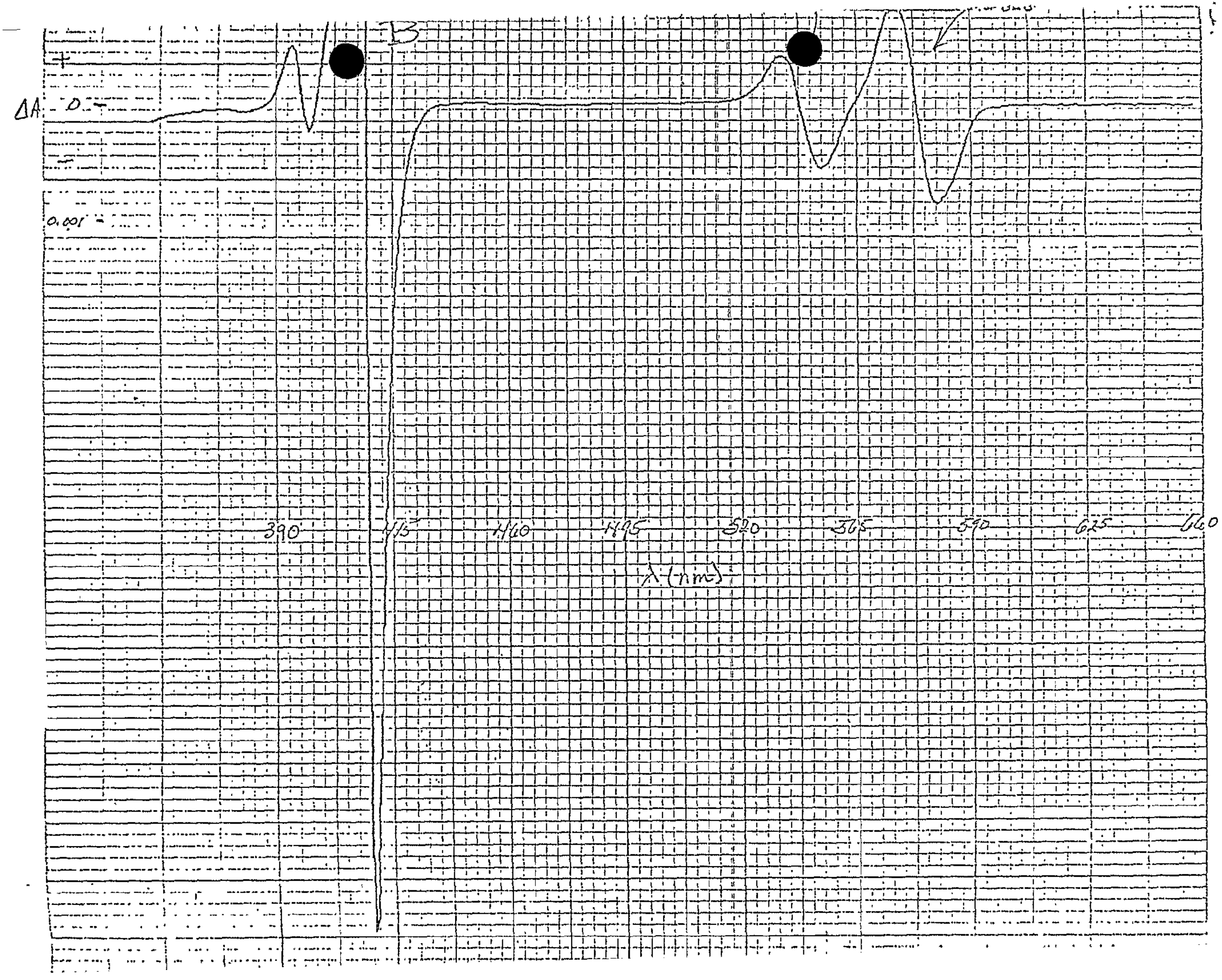


Fig. 1


+
ΔA 0 –
–
0.001 –
B
390
415
460
495
520
565
590
625
660
λ (nm)

Experimental

The magnetic circular dichrometer used in this project was built by G. H. Scott (Department of Chemistry). The computer interface was engineered by W. E. Reynolds (Genetics Department Instrumentation Research Laboratory) with programming assistance from R. A. Stillman. Reference spectra measurements were made by R. Records.

The light from a 450 watt xenon arc lamp was focused on the entrance slit of a Cary 15 monochromator. The exiting beam was collimated, linearly polarized by a Rochon prism, and circularly polarized by means of a Pockels modulator constructed from potassium dideuterium phosphate and driven at 1000 Hz. The beam of alternately left and right circularly polarized light was passed through the sample cell located in the hot hole of a 50,000 gauss superconducting magnet. In regions of absorption, the absorption coefficient of the sample for left and right circularly polarized light is different (the Faraday effect). This difference in light intensity is detected by a photomultiplier. The resulting 1,000 Hz signal is amplified and phase-sensitively detected by a Brower Lock-in-Voltmeter (model 131). The 10^{o} mv output of the Brower was monitored with an X-Y recorder and the 10 v output was connected to the computer interface. An electronic loop controls the voltage applied to the photomultiplier so that the gain of the photomultiplier is held constant as the stepping motor drives the monochromator through the spectyral region of interest.

The Brower has a rather wide range of sensitivity scales. These are calibrated for either circular dichroism or magnetic circular dichroism in the following manner: (1) The magnetic field is turned off and a standard solution of camphor sulfonic acid in a 1 cm. cuvette is placed in the sample compartment. The magnitude of the circular dichroism signal associated with the isolated $\underline{n\text{-}\pi^*}$ carbonyl absorption band at 290 nm is known from absolute measurements. (2) The loop gain is roughly optimized and a sensitivity setting on the Brower is chosen such that the signal meter (center zero) is approximately 90% of full scale. (3) The loop gain is then finely adjusted to the 90% reading. (4) The gain of the X-Y recorder is adjusted to give a deflection of 90% of full (zero center) scale. (5) The computer plots are scaled such that 1 inch = 1 X $10^{-5}\Delta$A.

As noted previously, the 10 v output signal from the Brower is connected to the computer interface. The signal goes to four operational amplifiers. The first is an integrator whose band pass is a sin x/x function (where $x = \pi T$); the second one is a high gain (X10) amplifier; the third one is a X1 amplifier; and the fourth one is a time integrator. The measurement cycle starts with the wavelength scanning system at rest at the long wavelength limit of the spectral region to be scanned. The signal and time integrators are also at rest. The first step of the cycle is to release the integrator resets on both the signal and time integrators. At some time T, depending on the signal strength, either the signal integrator reaches a preset absolute threshold or the time integrator reaches that threshold. At that time the integrators are converted to hold amplifiers. The computer is then called upon to read four values via an analog-to-digital converter.. After the time of integration, the integrated signal, the high gain amplifier, and the low gain amplifier values are read: the integrators are then reset and held. The stepping motor is given a set number of pulses (21) resulting in an increment of scan of approximately 1.05 nm. At this point the measurement cycle at a particular wavelength has been completed. The measurement scan is completed after the stepping motor har driven the monochromator to the short wavelength limit desired.

Although several sampling modes have been incorporated, the most secure and conservative one was used for the lunar sample measurements. In this mode data was taken at 300 discrete wavelengths in steps of 1.05 nm. At each wavelength position 16 cycles of data were taken. The analog-to-digital converter readings were immediately converted to nanoseconds and the simple average was filed. A separate data point was recorded for the average of the integrated signal divided by time and the X1 amplifier output. The high gain amplifiers were often in saturation and no record was made of those readings.

The sensitivity enhancement achieved permits the use of a sensitivity scale of $5 \times 10^{-5} \Delta A$. Since the maximum sensitivity scale available to us at the start of this project was $1 \times 10^{-3} \Delta A$, a sensitivity increase of 20 has been achieved. It should be appreciated however that although the 5×10^{-5} scale provides useful information for relatively strong signals, the credibility given to very weak signals is limited by such factors as the small changes in cell position obtaining between the sample measurement and the solvent baseline measurement and by source arc wander during very slow scans.

Under the conditions used for these measurements the detection limit, relative to Mg(II) deuteroporphyrin IX dimethyl ester, is 22 ng./ml. This limit is based on the condition imposed of observing both A terms. The detection limit based on observing the A term associated with the B band is 3 ng./ml. Data obtained for establishing this detection threshold will be found in Appendix A. During these measurements the detection limit in the Q region was degraded (1/3) by the necessity of using a wider than optimal slit width in order to avoid overloading the Brower. If an A term had been detected in the B region, a noise limiting circuit of the Brower would have been energized. The slit width of the monochromator would have been reduced and the scan repeated. Under these conditions the detection limit is 7 ng/ml.

Results

The MCD results obtained on the lunar extract sample ARC are shown in Figures 2a-2d. The corresponding computer recorded data are collected in the appendiz. This data as well as all other recorded data are on permanent computer files.

The instrument was adjusted to give the best possible solvent baseline (minimum slope) on October 7. The baseline was again measured on October 8, prior to the arrival of the lunar sample. Sample ARC was placed in the cell and the MCD spectrum was recorded (Figure 2a) during an eighty-minute scan. The cell was emptied and filled with methanol. The baseline data obtained are shown in the computer plot presented in Figure 2b. It will be noted that neither the sample nor the baseline curves are flat. This feature is a characteristic of the particular photomultiplier tube used and does not degrade the information obtained. The raw data MCD curve of the sample corrected for solvent baseline is shown in Figure 2c and the smoothed difference curve is shown in Figure 2d. The data and computer plots obtained from the X1 analog channel are collected in the appendiz and when compared with the data taken from the integrator channel, Figures 2a-2d, reflect the extremely conservative data handling techniques used.

The same procedure was followed for the sand blank sample. The MCD results are presented in Figures 3a-3d and the corresponding computer recorded data are collected in the appendix. In the smoothed sand blank MCD curve shown in Figure 4d it will be noted that the observed signal does not average about zero. This may have been caused by a very gradual movement of the arc during the time required to scan the sample and the solvent blank. The lunar extract MCD curve (Figure 3d) does not, however, exhibit this feature.

Discussion and Evaluation

The criteria established for the detection of a metalloporphyrin are:

(1). The observation of an S-shaped A term around 570 nm. The long wavelength lobe will be negative with respect to the sign convention adopted.[4]

(2). The observation of a second S-shaped A term at about 400 nm.
The long wavelength lobe of this A term will also be negative.[4]

A critical examination of the MCD curve of the lunar extract ARC shown in Figure 3d reveals that:

(1). The A term in the vicinity of 570 nm is definitely not present.

(2). There is an apparent A term around 400 nm. As noted in a previous section some metalloporphyrins exhibit a significantly more intense A term in the B band than in the Q band. However, the wabelength separation (23 nm) between the maximum of the negative lobe at 424 nm and the positive lobe at 401 nm is twice that observed in the reference metalloporphyrin spectra collected for this project. Furthermore, the approximately equal spacing between the positive and negative signals in the 335-475 nm region strongly suggests that these signals are actually instrumental artifacts.

On the basis of the criteria established, we conclude that the amount of metalloporphyrins present in the lunar extract ARC is less than 7ng./ml.

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5. G. W. Hodgson and E. Bunnenberg (unpublished results).

Figure 2a. Magnetic circular dichroism curve of the lunar extract ARC from the integrated signal divided by time.

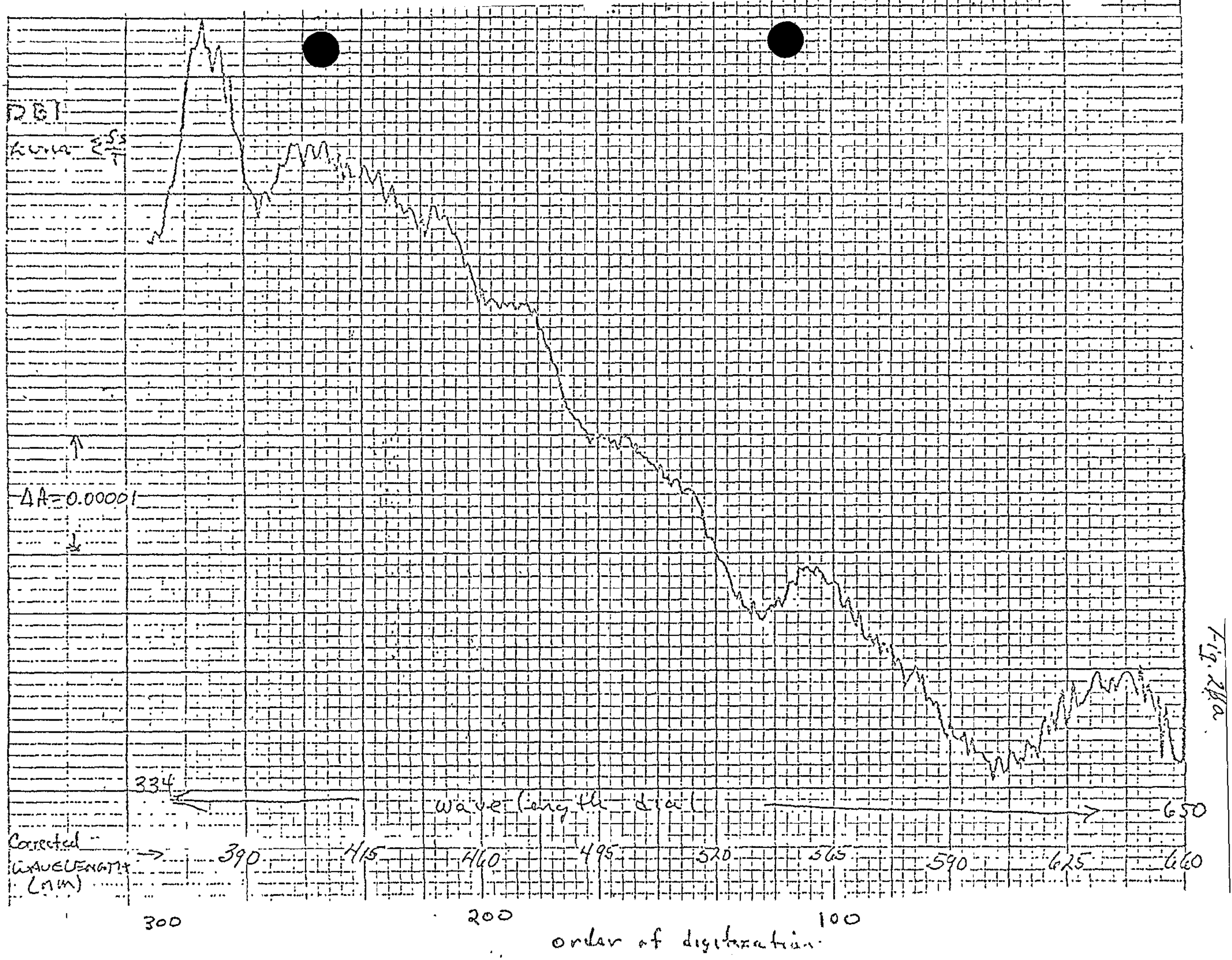
DBI
Kuna ε 55/1
ΔA=0.00001
334
wave length dial
650
Corrected WAVELENGTH (nm)
390
415
460
495
520
565
590
625
660
300
200
100
order of digitization

Fig. 28a

Figure 2b. Methanol baseline for lunar sample ARC from the integrated signal divided by time.

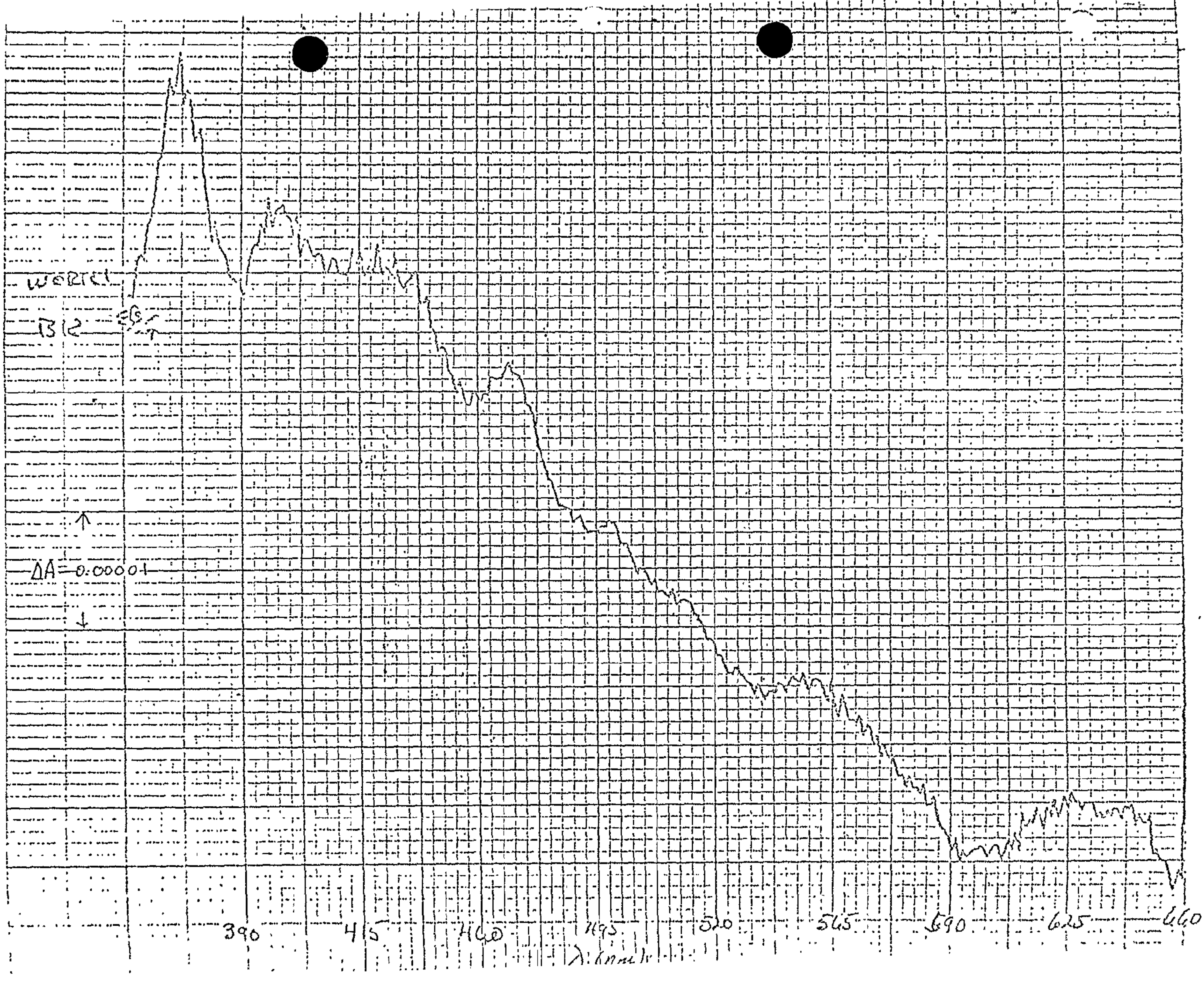

FIGURE 2b.

Figure 2c. Magnetic circular dichroism curve of the lunar extract sample ARC corrected for the solvent baseline.

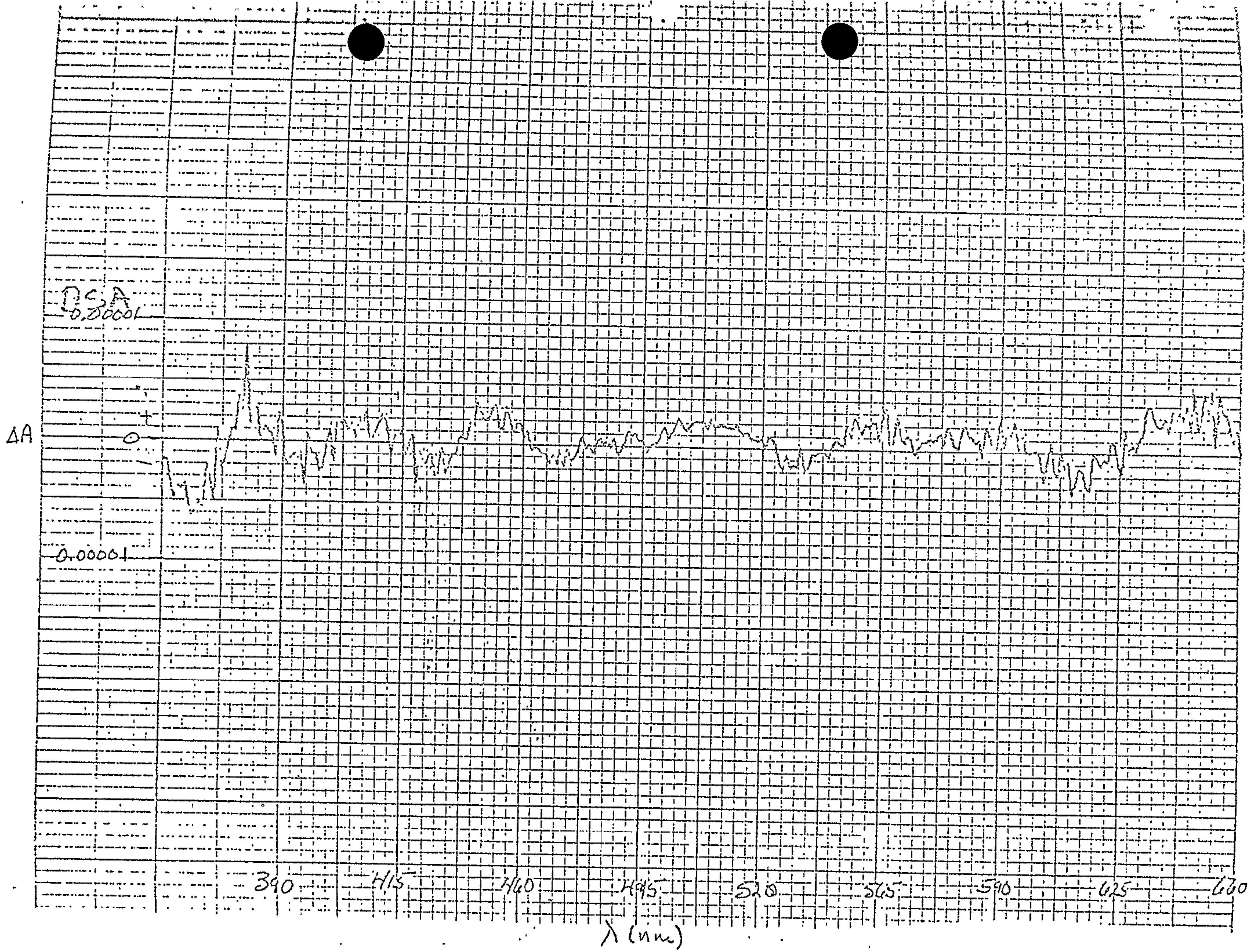

Fig. 3C

Figure 2d. Smoothed (21 point) magnetic circular dichroism curve of the lunar extract sample ARC corrected for the solvent baseline.

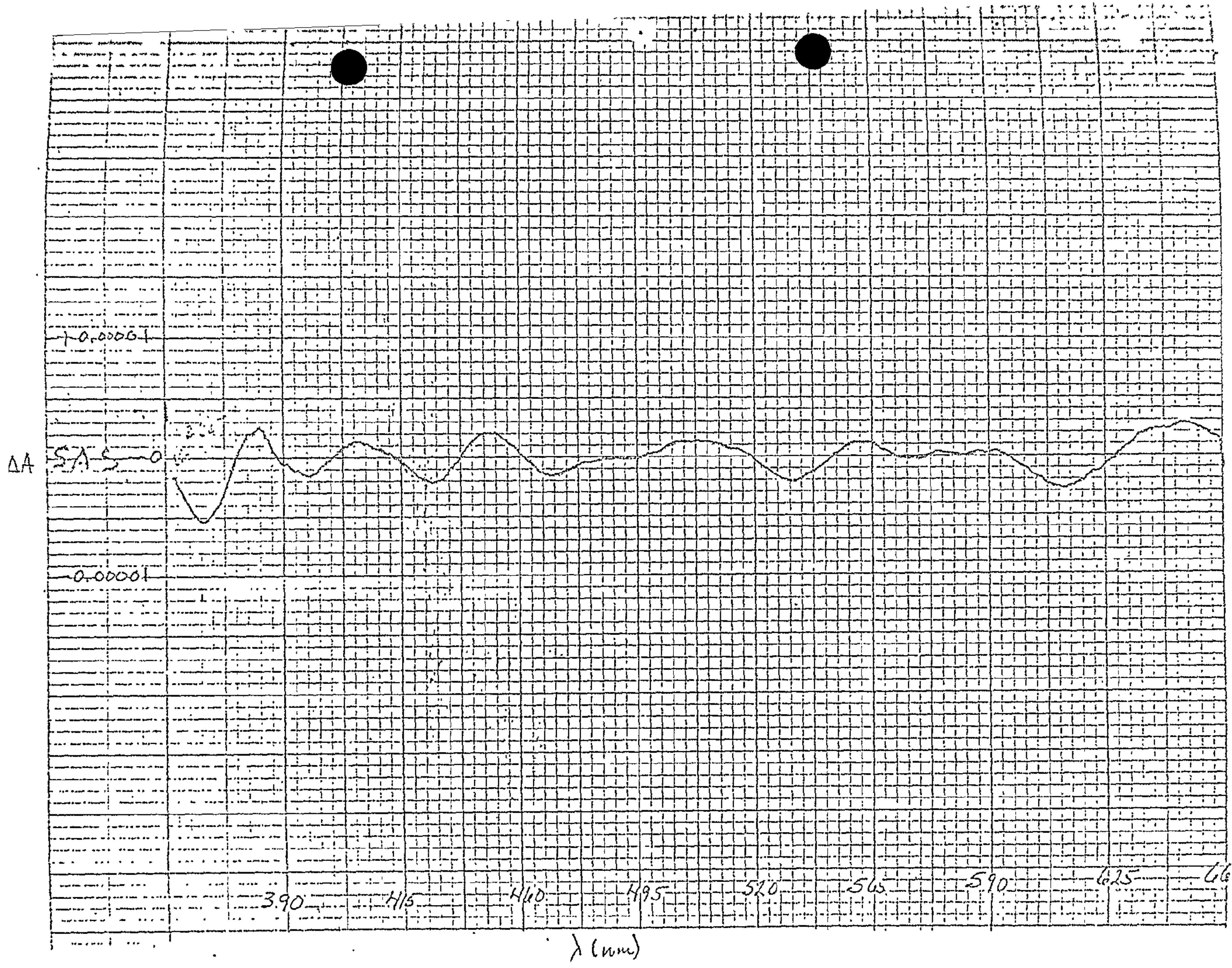

Fig 10.

Figure 3a. Magnetic circular dichroism curve of the sand blank sample from the integrated signal divided by time.

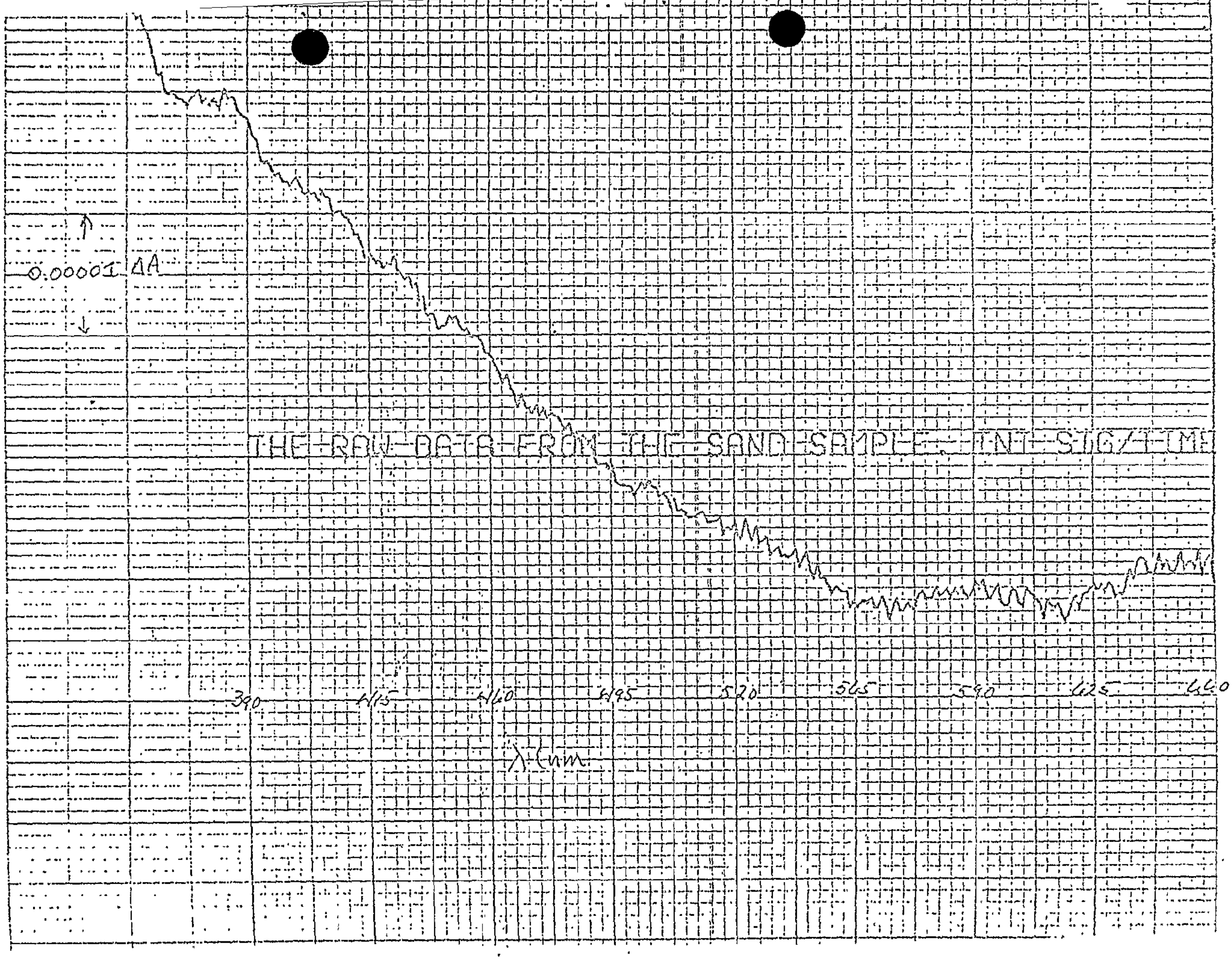
0.00001 ΔA
THE RAW DATA FROM THE SAND SAMPLE. INT SIG/TIME
390
415
460
495
520
565
590
625
660
λ (nm

Fig 3a

Figure 3b. The corresponding solvent baseline.

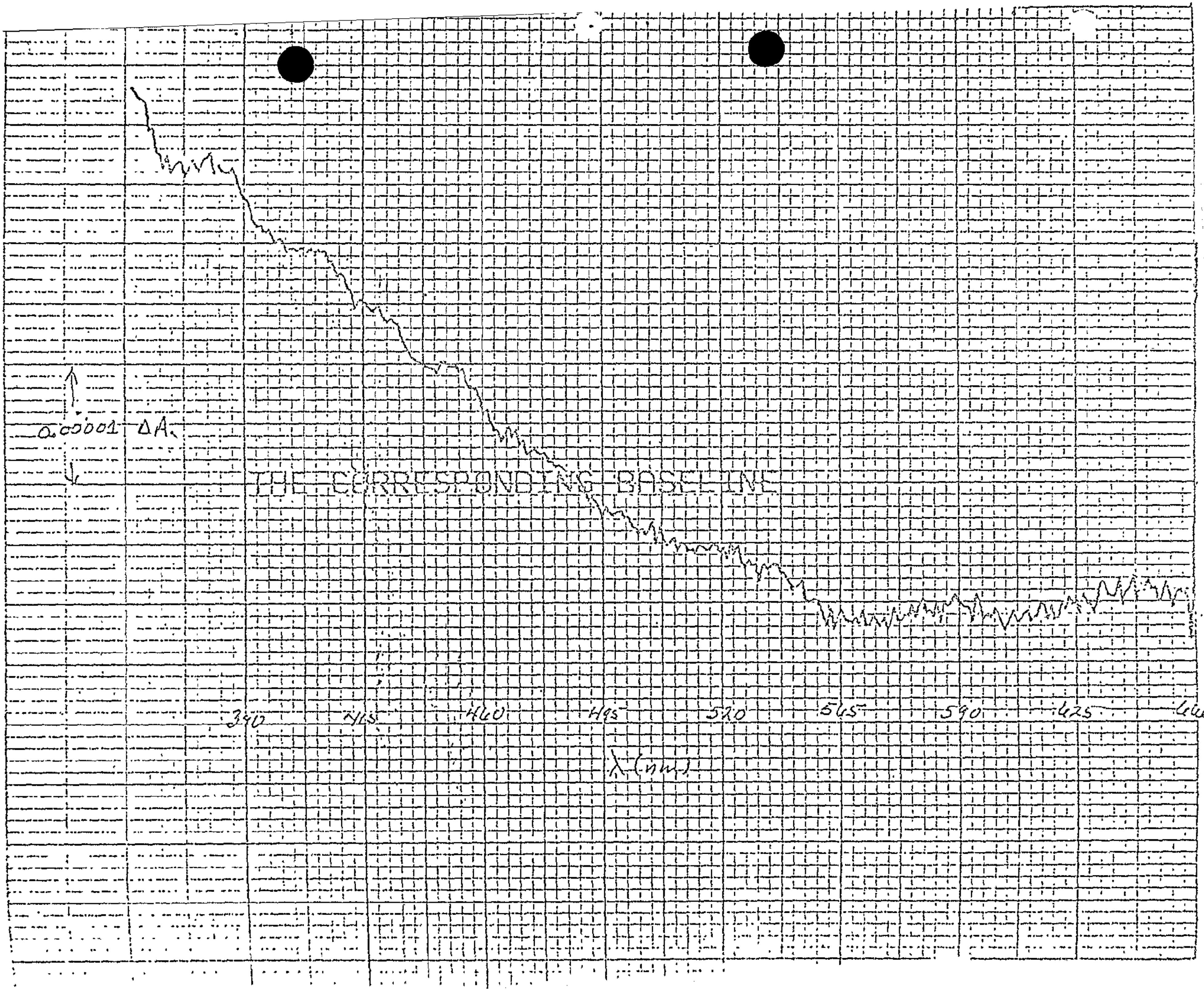
0.00001 ΔA.
THE CORRESPONDING BASELINE
390
425
460
495
520
565
590
625
660
λ (nm)

Fig 3b.

Figure 3c. Magnetic circular dichroism curve of the sand blank sample corrected for the solvent baseline.

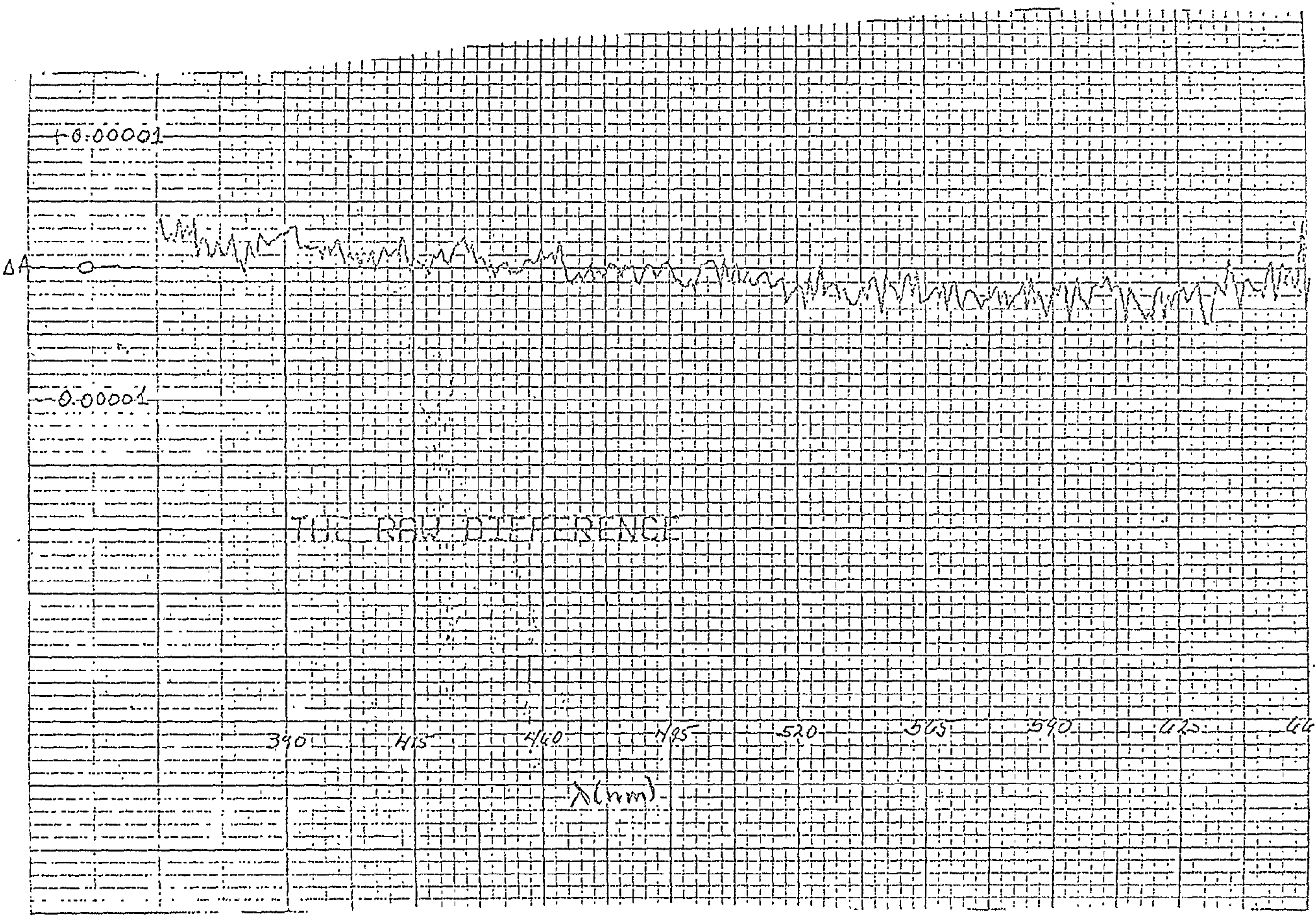
+0.00001
ΔA — 0
-0.00001
THE RAW DIFFERENCE
390
415
450
485
520
555
590
625
660
λ(nm)

Figure 3d. Smoothed (21 point) magnetic circular dichroism curve of the sand blank sample corrected for the solvent baseline.

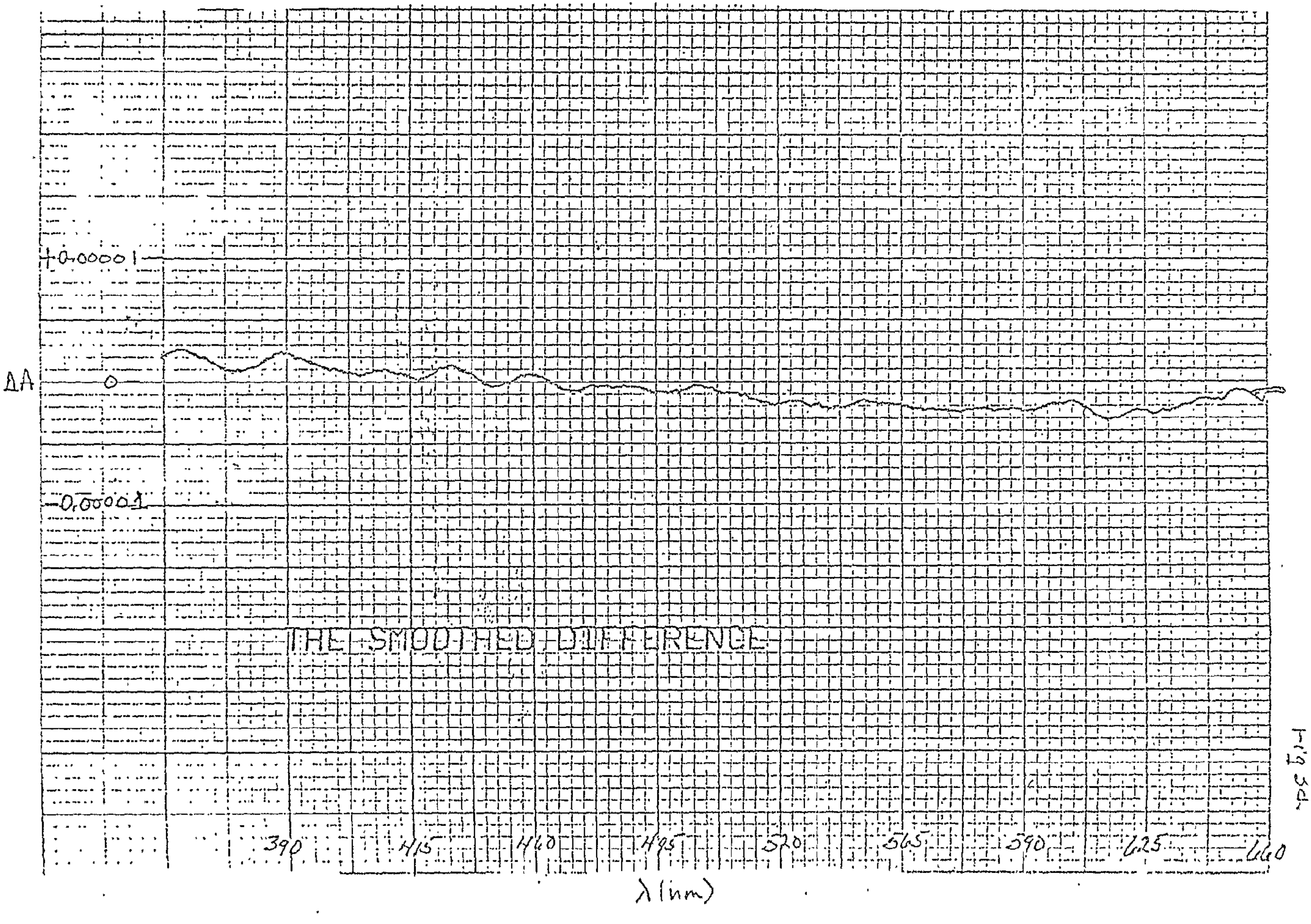
ΔA
+0.00001
0
-0.00001
THE SMOOTHED DIFFERENCE
390
415
440
495
520
565
590
625
660
λ(nm)

Fig 3d.

Appendix A

A1. Digital recorded values for the lunar sample ARC plotted in Figure 2a. (LUNA08_3)

A2. Digital recorded values for the methanol blank. The five wild points indicate errors in recording or digitizing. (LUNA08_4)

A3. Digital recorded values for the methanol blank plotted in Figure 2b. The wild points have been eliminated by taking the average of the adjoining values. (LUNPAC_4)

A4. Digital values for the plot (Figure 2c) of the MCD curve of the lunar sample ARC corrected for the methanol baseline.

A5. Computer plot and digital recorded values taken from the Xi analog channel for the lunar sample ARC. (LUNA08_3)

A6. Computer plot and digital recorded values taken from the X1 analog channel for the methanol blank. The wild points were eliminated by taking the average of the adjoining values. (LUNPAC _4)

A7. Computer plot and digital recorded values taken from the X1 analog channel for the lunar sample ARC corrected for the methanol baseline.

A8. The smoothed difference plot corresponding to A7.

A9. This plot reflects the extremely conservative data handling techniques used. This plot is the difference between the data derived from the integrator channel and the X1 analog channel. The negligible difference between the two data channels indicates that the scanning time could have been decreased without degrading the information.

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-4.0278E 02-4.3490E 02-3.7177E 02-4.2023E 02-3.9978E 02-3.85
-3.9222E 02-4.1711E 02-4.0800E 02-4.0909E 02-3.7925E 02-3.88
-4.4061E 02-3.9935E 02-4.5649E 02-4.7214E 02-4.1304E 02-4.38
-4.8000E 02-5.2924E 02-5.0765E 02-5.1074E 02-4.9709E 02-5.33
-5.4814E 02-5.5236E 02-5.2507E 02-5.3090E 02-5.6435E 02-5.34
-4.9390E 02-5.2264E 02-4.8219E 02-4.9576E 02-4.9513E 02-4.92
-4.3016E 02-4.3938E 02-4.2452E 02-4.2982E 02-3.8590E 02-3.90
-3.6919E 02-3.5923E 02-3.7110E 02-3.3465E 02-3.4845E 02-3.33
-3.3305E 02-3.2548E 02-2.8521E 02-3.0862E 02-2.9403E 02-2.61
-2.3704E 02-2.3841E 02-2.2709E 02-2.1581E 02-2.0400E 02-2.20
-2.4145E 02-2.3204E 02-2.3517E 02-2.6130E 02-2.7626E 02-2.80
-2.9966E 02-2.9094E 02-2.6722E 02-2.8828E 02-2.7286E 02-2.74
-2.0953E 02-1.9820E 02-1.9440E 02-1.8014E 02-1.6151E 02-1.55
-8.6100E 01-7.7398E 01-6.8130E 01-6.5451E 01-6.6951E 01-7.32
-4.6328E 01-2.3756E 01-3.4831E 01-2.4783E 01-2.0980E 01-1.23
 2.7179E 01 1.9406E 01 3.6917E 01 3.6594E 01 3.6404E 01 1.497
 4.1758E 01 3.5977E 01 3.9782E 01 2.4892E 01 4.8237E 01 5.378
 8.9999E 01 1.0920E 02 1.2722E 02 1.5992E 02 1.6414E 02 1.877
 2.5131E 02 2.6877E 02 2.7131E 02 2.7125E 02 2.5986E 02 2.701
 2.7340E 02 2.8188E 02 2.7797E 02 2.6922E 02 2.9759E 02 2.712
 3.6517E 02 3.7846E 02 3.9159E 02 3.8899E 02 3.9920E 02 4.211
 4.0981E 02 3.8522E 02 4.2268E 02 3.9560E 02 4.2313E 02 4.357
 4.7273E 02 4.5946E 02 4.4109E 02 4.7333E 02 4.9444E 02 4.823
 4.7942E 02 4.8704E 02 4.8437E 02 5.1079E 02 4.8183E 02 5.24
 5.4450E 02 5.2120E 02 5.1790E 02 5.3844E 02 5.4031E 02 5.053
 5.1051E 02 5.0383E 02 5.0761E 02 4.7786E 02 4.7263E 02 4.4322
 4.6050E 02 4.7421E 02 4.8334E 02 5.4436E 02 5.5856E 02 5.712
 7.0283E 02 6.6411E 02 7.1086E 02 7.1108E 02 7.5854E 02 7.190
 5.3704E 02 5.1368E 02 4.7543E 02 4.7366E 02 4.4614E 02 3.9741
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DBl 300 recorded readings of the lunar

the maximum and min points are noted

File name LUNA08_3

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put list(DB2)!
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909E 02-3.7925E 02-3.8813E 02-4.1065E 02-4.1882E 02-4.3551E 02-4.3763E 02
214E 02-4.1304E 02-4.3825E 02-4.8140E 02-4.4856E 02-4.8840E 02-4.5955E 02
074E 02-4.9709E 02-5.3358E 02-5.2049E 02-5.3954E 02-5.2060E 02-5.1602E 02
090E 02-5.6433E 02-5.3412E 02-5.3088E 02-5.1915E 02-5.1820E 02-5.1991E 02
576E 02-4.9513E 02-4.9270E 02-4.6852E 02-4.9414E 02-4.8106E 02-4.5745E 02
982E 02-3.8598E 02-3.9840E 02-3.7114E 02-3.8363E 02-3.9176E 02-4.0572E 02
465E 02-3.4845E 02-3.3309E 02-3.5667E 02-3.2446E 02-3.4113E 02-3.2272E 02
862E 02-2.9403E 02-2.6148E 02-2.7757E 02-2.7796E 02-2.3874E 02-2.3596E 02
581E 02-2.0400E 02-2.2007E 02-2.1482E 02-2.0983E 02-2.1648E 02-2.1092E 02
130E 02-2.7626E 02-2.6087E 02-2.7719E 02-2.7481E 02-2.8000E 02-2.9282E 02
828E 02-2.7286E 02-2.7491E 02-2.5103E 02-2.6019E 02-2.4853E 02-2.2618E 02
014E 02-1.6151E 02-1.5568E 02-1.5542E 02-1.2282E 02-1.1037E 02-9.8231E 01
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783E 01-2.0980E 01-1.2354E 01-8.8316E 00 1.6963E 00 3.5616E 00 9.1905E 00
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992E 02 1.6414E 02 1.8773E 02 2.0198E 02 2.2953E 02 2.2834E 02 2.6393E 02
125E 02 2.5986E 02 2.7012E 02 2.7274E 02 2.6715E 02 2.7275E 02 2.6275E 02
922E 02 2.9759E 02 2.7128E 02 2.9891E 02 3.1891E 02 3.3760E 02 3.3280E 02
899E 02 3.9920E 02 4.2114E 02 4.1667E 02 4.1059E 02 4.3703E 02 4.3419E 02
560E 02 4.2313E 02 4.3575E 02 4.2720E 02 4.2559E 02 4.4046E 02 4.3525E 02
7333E 02 4.9444E 02 4.8238E 02 4.7487E 02 4.8808E 02 5.0749E 02 4.8872E 02
1079E 02 4.8183E 02 5.2404E 02 4.9702E 02 5.1714E 02 5.0889E 02 5.4328E 02
5844E 02 5.4031E 02 5.0536E 02 5.2070E 02 5.4282E 02 5.3866E 02 5.4173E 02
7786E 02 4.7263E 02 4.4322E 02 4.6134E 02 4.5717E 02 4.1785E 02 4.5080E 02
4436E 02 5.5856E 02 5.7124E 02 6.6353E 02 6.1689E 02 6.7474E 02 7.1462E 02
1108E 02 7.5854E 02 7.1908E 02 7.0973E 02 7.0905E 02 6.6445E 02 6.0871E 02
7366E 02 4.4614E 02 3.9741E 02 3.8665E 02 3.9908E 02 3.7776E 02 3.8146E 02
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dings of the lunar sample.

nts are noted

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FOLDOUT FRAME 2

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   -453   -464   -455   -468   -459   -467   -443   -507   -442   -454
   -439   -440   -424   -450   -430   -456   -487   -437   -466   -449
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   -507   -523   -543   -518   -515   -523   -535   -522   -517   -522
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   -268   -256   -272   -256   -252   -244   -239   -224   -225   -234
   -232   -222   -203   -203   -180   -175   -177   -155   -145   -132
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    447    468    472    452    447    479    481    475    480    499
    505    476    545    509    538    542    562    550    550    521
    574    512    530    492    495    479    438    402    438    430
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(LUNA08_4)

The original data set
with wild points

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  -439   -440   -424   -450   -430   -456   -467   -437   -466   -449
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     9     23     38     33     26     48     50     55     54     72
    96     99    124    136    162    203    223    225    259    270
   277    280    296    281    268    268    268    270    241    243
   231    238    249    225    225    239    264    245    272    284
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   437    430    421    434    471    443    452    457    447    496
   451    454    456    443    482    462    487    459    445    445
   447    468    472    452    447    479    481    475    480    499
   505    476    545    509    538    542    562    556    550    521
   574    512    530    492    495    479    438    402    438    430
   437    441    477    485    492    533    497    561    592    688
   676    665    733    751    728    814    770    742    771    706
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A4

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 4.1445E 00-6.1419E 01-5.6942E 01-3.1398E 01-2.7712E 01-5.1393E 01-
-4.0336E 01-2.8826E 01 1.8876E 01-1.2515E 01-4.9331E 01-1.0331E 01 5.
 2.9049E 01 5.3552E 00 5.2778E 01 2.6263E 01 4.4920E 01 1.1805E 01 5.
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 8.9777E 00 1.0575E 01 1.7850E 01 1.0246E 01-1.5543E 01-6.1025E 00-5.
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 4.5872E 01 3.6135E 01 4.0821E 01 4.1059E 01 4.4061E 01 4.2329E 01 3.
 4.8640E 01 4.8746E 01 4.6160E 01 4.1621E 01 3.3765E 01 4.2953E 01 5.4
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-2.6635E 01-1.1722E 01-2.5321E 01-9.8840E 00-8.9915E 00 1.9680E 00 4.
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 2.1559E 01 5.4573E 00-1.5377E 01 2.9418E 01 1.2140E 01 2.0357E 01-1.2
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 2.3191E 01 3.2919E 01 6.1294E 00 5.9254E 01 6.5833E 01 3.7050E 01 1.6
 2.6189E 01-1.6675E 00-2.2135E 01-4.0337E 01 2.9907E 01-9.5493E 01-
-1.0474E 02-1.2148E 02-9.7651E 01-6.5899E 01-7.5606E 01-7.1614E 01-9.0
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FOLDOUT FRAME

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9E 01 7.2785E 01 6.1711E 01 7.4195E 01 3.8588E 01
0E 01 3.2606E 01 2.4185E 01 6.7258E 00 1.6917E 01
1E 01-1.4100E 01-1.6594E 01-2.1667E 01-9.6333E 00
3E 01-6.9813E 01-1.5792E 01-2.7885E 01 5.6177E 00
1E 01 5.6674E 00 3.0029E 00-8.3643E-01 2.6536E 00
5E 01 5.3574E 01 9.3733E 00 7.0884E 00 2.7576E 01
7E 01 4.5441E 01 3.4353E 01 4.6277E 00 1.0833E 01
2E 01 2.0177E 01 1.6701E 01 1.6961E 01 7.6079E 00
1E 01 2.9492E 01-3.7898E 00 7.3068E 01 6.1655E 01
7E 01 4.5519E 01 5.5693E 01 2.2161E 01 4.3454E 01
5E 00-5.7368E 00-5.6042E 00-1.0422E 01-9.8604E 00
0E 01-1.1400E 01-3.6150E 01-2.2913E 01 8.2022E 00
2E 01 2.2504E 01 3.2836E 01 2.9487E 01 3.4180E 01
9E 01 3.8637E 01 5.4100E 01 3.6120E 01 4.8875E 01
3E 01 5.4475E 01 4.1734E 01 3.1637E 01 2.0777E 01
4E 00 1.4187E 01 1.6243E 01 2.8459E 01 2.4117E 01
8E 00 1.4589E 01 1.0935E 01 2.1242E 01 1.0991E 01
1E 01-2.1165E 01 3.5890E 00-3.1438E 01-6.1047E 00
0E 00 4.4629E 00-2.9417E 00 3.1046E 01 1.8966E 01
9E [illegible] 3.4532E 01 7.2919E 01 6.4913E 01 4.7950E 01
9E [illegible] 1.6812E 01 1.9837E 01-1.3345E 01-1.2094E 01
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7E 01-1.2859E 01 2.8214E 01 6.1690E 01 4.3055E 01
1E 01 1.5653E 01 4.2115E 01 2.7957E 01 4.3866E 01
1E 01-4.1818E 01-1.3227E 01-1.3611E 01 2.0678E 01
3E 01 2.3028E 01 5.4547E 01-2.0451E 01 2.0077E 01
0E 01 1.6623E 02 5.4932E 01 8.2664E 01 2.5904E 01
3E 01-9.1133E 01-3.3515E 01-1.0665E 02-9.7554E 01
4E 01-9.0901E 01-6.7170E 01-2.6405E 01-2.6847E 01
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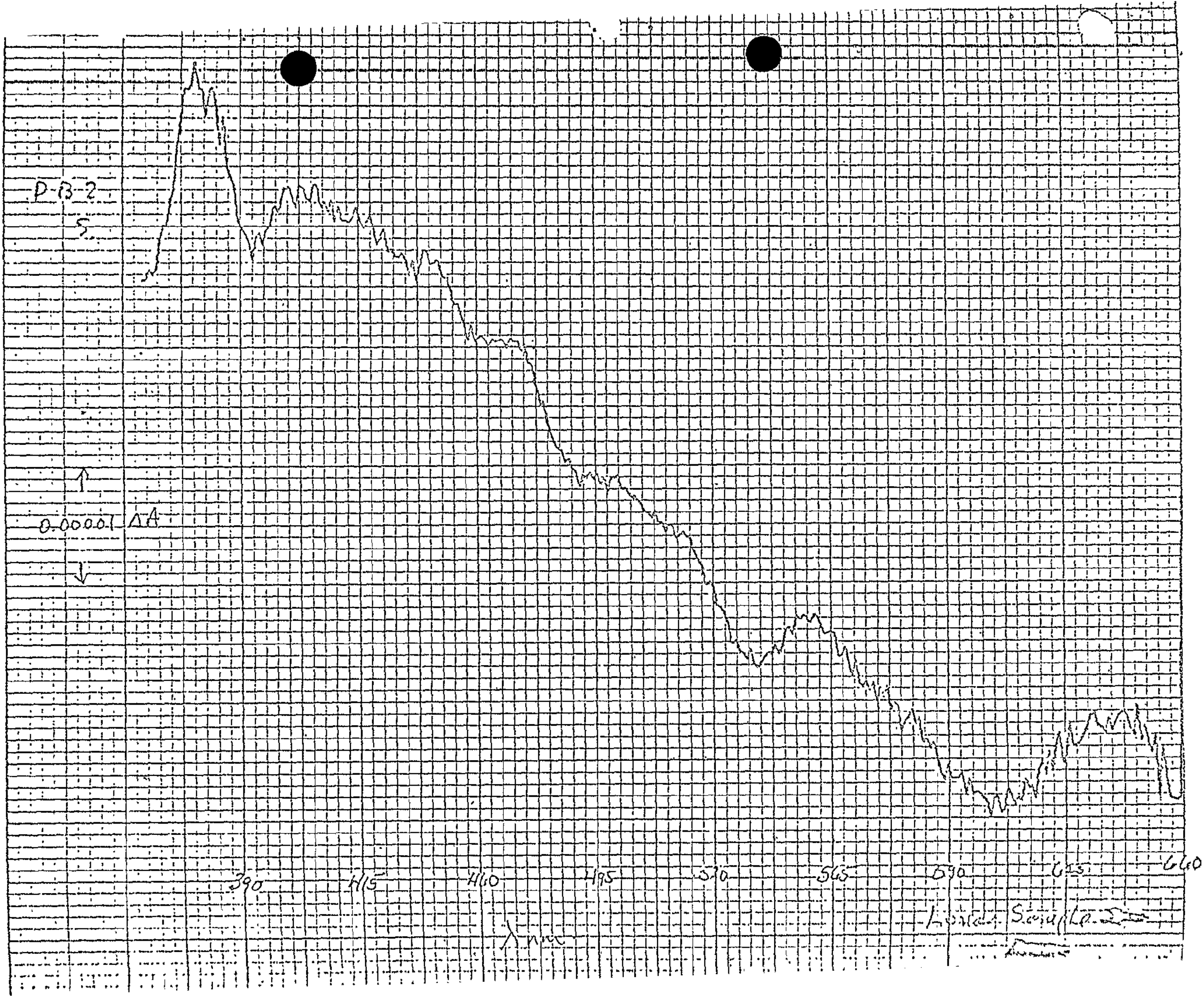
FOLDOUT FRAME 2


P-B-2
5
0.00001 ΔA
390
415
460
495
530
565
590
625
660
λ nm
Loaded Sample

A5

DB2

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-3.8367E 02-4.0895E 02-3.9932E 02-3.9633E 02-3.7365E 02-3.7810E 02-3.
-4.3067E 02-3.8865E 02-4.4351E 02-4.6047E 02-4.0749E 02-4.3067E 02-4.
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-5.3594E 02-5.4358E 02-5.1248E 02-5.1920E 02-5.5155E 02-5.2301E 02-5.
-4.8510E 02-5.1134E 02-4.7277E 02-4.8540E 02-4.8418E 02-4.8425E 02-4.
-4.2285E 02-4.3266E 02-4.1500E 02-4.2278E 02-3.7944E 02-3.9281E 02-3.
-3.6366E 02-3.5509E 02-3.6661E 02-3.2786E 02-3.4613E 02-3.2889E 02-3.
-3.2946E 02-3.2324E 02-2.8345E 02-3.0848E 02-2.8996E 02-2.6042E 02-2.
-2.3653E 02-2.3869E 02-2.2511E 02-2.1143E 02-2.0492E 02-2.1567E 02-2.
-2.3884E 02-2.2650E 02-2.3308E 02-2.5892E 02-2.7375E 02-2.5786E 02-2.7
-2.9579E 02-2.8850E 02-2.6237E 02-2.8160E 02-2.7353E 02-2.6710E 02-2.
-2.0936E 02-1.9532E 02-1.9102E 02-1.7957E 02-1.5938E 02-1.5085E 02-1.5
-9.1688E 01-7.5974E 01-7.3236E 01-6.5664E 01-7.0535E 01-7.4659E 01-5.
-4.6857E 01-2.7766E 01-4.1311E 01-3.0859E 01-3.0503E 01-1.4890E 01-
 1.6283E 01 1.5074E 01 3.7045E 01 3.2245E 01 3.3419E 01 1.1601E 01 3.
 4.2555E 01 3.3774E 01 3.6938E 01 1.9553E 01 4.3337E 01 4.8101E 01 6.2
 8.9555E 01 1.0463E 02 1.2415E 02 1.6041E 02 1.5550E 02 1.8569E 02 1.
 2.4225E 02 2.6155E 02 2.5971E 02 2.6408E 02 2.4908E 02 2.6195E 02 2.
 2.6141E 02 2.6870E 02 2.6749E 02 2.5963E 02 2.8722E 02 2.6234E 02 2.
 3.4898E 02 3.6103E 02 3.7532E 02 3.7333E 02 3.8083E 02 4.0248E 02 3.
 3.9153E 02 3.6935E 02 4.0273E 02 3.7788E 02 4.0216E 02 4.1595E 02 4.
 4.5431E 02 4.4187E 02 4.2637E 02 4.5421E 02 4.7526E 02 4.6438E 02 4.5
 4.6324E 02 4.6697E 02 4.6715E 02 4.9150E 02 4.6420E 02 5.0142E 02 4.8
 5.2709E 02 4.9829E 02 5.0103E 02 5.2012E 02 5.2211E 02 4.8699E 02 5.0
 4.9271E 02 4.8567E 02 4.9492E 02 4.6331E 02 4.5666E 02 4.3188E 02 4.5
 4.4717E 02 4.5983E 02 4.6765E 02 5.2645E 02 5.4099E 02 5.5028E 02 6.4
 6.7900E 02 6.3968E 02 6.8519E 02 6.8455E 02 7.2835E 02 6.9376E 02 6.8
 5.1937E 02 4.9275E 02 4.5616E 02 4.5773E 02 4.3444E 02 3.8481E 02 3.7
```

LUNAD 8-3

FOLDOUT FRAME

```
                                   02-4.8223E 02-4.2075E 02
310E 02-3.7398E 02-3.7759E 02-3.8783E 02-4.0458E 02
810E 02-3.9949E 02-4.0991E 02-4.2403E 02-4.2964E 02
067E 02-4.7223E 02-4.3974E 02-4.7902E 02-4.5232E 02
218E 02-5.1685E 02-5.2848E 02-5.1244E 02-5.0380E 02
301E 02-5.1792E 02-5.0903E 02-5.0771E 02-5.1074E 02
425E 02-4.5031E 02-4.8720E 02-4.7230E 02-4.4742E 02
281E 02-3.6615E 02-3.7959E 02-3.8744E 02-4.0252E 02
889E 02-3.5232E 02-3.2125E 02-3.3593E 02-3.1929E 02
342E 02-2.7442E 02-2.7681E 02-2.3628E 02-2.3418E 02
067E 02-2.1054E 02-2.0780E 02-2.1384E 02-2.0808E 02
786E 02-2.7250E 02-2.7119E 02-2.7716E 02-2.8818E 02
710E 02-2.4705E 02-2.5469E 02-2.4733E 02-2.2373E 02
185E 02-1.5220E 02-1.2269E 02-1.1064E 02-9.8336E 01
559E 01-5.4607E 01-5.3896E 01-6.4846E 01-4.7355E 01
30E 01-8.4258E 00 2.8441E-01-2.8797E 00 5.0483E 00
01E 01 3.3270E 01 2.3571E 01 4.0173E 01 3.0432E 01
01E 01 6.2571E 01 5.9905E 01 7.6472E 01 8.0631E 01
69E 02 1.9521E 02 2.2177E 02 2.2291E 02 2.5608E 02
95E 02 2.6312E 02 2.5885E 02 2.6305E 02 2.5043E 02
34E 02 2.8765E 02 3.0557E 02 3.2313E 02 3.2089E 02
48E 02 3.9985E 02 3.9402E 02 4.1770E 02 4.1812E 02
95[illegible]2 4.0742E 02 4.0888E 02 4.2260E 02 4.1645E 02
38[illegible]2 4.5567E 02 4.6807E 02 4.8844E 02 4.7198E 02
42E 02 4.8165E 02 4.9861E 02 4.8923E 02 5.2407E 02
99E 02 5.0224E 02 5.2332E 02 5.1749E 02 5.2233E 02
38E 02 4.5008E 02 4.4283E 02 4.0557E 02 4.3768E 02
28E 02 6.4306E 02 5.9556E 02 6.5070E 02 6.9045E 02
0E 02 6.8398E 02 6.8476E 02 6.3566E 02 5.8664E 02
1E 02 3.7308E 02 3.8218E 02 3.6455E 02 3.6494E 02
```

FOLDOUT FRAME 2


WORK-2
BK
↑
0.0002 ΔA
↓
390
425
460
495
460
520
495
555
520
590
Background
625
660
λ (nm)

			[illegible]	[illegible]	[illegible]	-532	-528	-519	-523
-462	-470	-471	-457	-477	-440	-447	-438	-465	-446
-443	-461	-446	-459	-453	-461	-437	-506	-434	-447
-434	-433	-420	-445	-422	-447	-459	-432	-455	-447
-478	-462	-442	-472	-463	-474	-451	-514	-484	-509
-498	-513	-530	-507	-506	-514	-522	-511	-500	-511
-512	-632	-524	-509	-528	-493	-510	-491	-478	-473
-462	-421	-439	-437	-401	-417	-410	-411	-389	-407
-385	-303	-376	-362	-366	-347	-371	-333	-351	-326
-321	-339	-309	-320	-311	-313	-296	-273	-310	-296
-251	-284	-270	-255	-249	-247	-258	-265	-239	-253
-250	-241	-253	-272	-262	-255	-269	-265	-271	-285
-269	-256	-270	-253	-253	-245	-238	-225	-226	-233
-232	-223	-206	-202	-182	-177	-177	-159	-144	-133
-135	-112	-106	-109	-111	-114	-93	-106	-97	-97
-99	-74	-83	-72	-58	-62	-66	-47	-32	-18
-15	-12	21	145	26	11	11	1	4	5
2	193	33	29	21	44	47	48	47	66
96	91	116	129	154	194	212	216	251	260
266	270	286	271	257	256	257	260	232	234
220	229	238	214	213	228	252	233	262	271
302	305	300	332	341	392	383	371	433	430
420	410	401	414	451	424	431	436	427	473
428	-511	437	424	461	439	464	439	427	424
427	449	449	430	428	455	459	454	459	478
484	454	520	486	512	516	537	533	524	500
549	489	504	470	472	453	419	386	420	416
419	426	460	465	471	512	481	538	571	662
649	638	706	716	700	779	739	711	737	677

WORK2

(28) = -436.5

(62) = -518

(164) = -23.5

(172) = 18

(232) = 433

Work 2 with original 'wild' Points and corrected values.

The plot is of the corrected values.


DSS
390
415
460
495
520
565
590
625
660

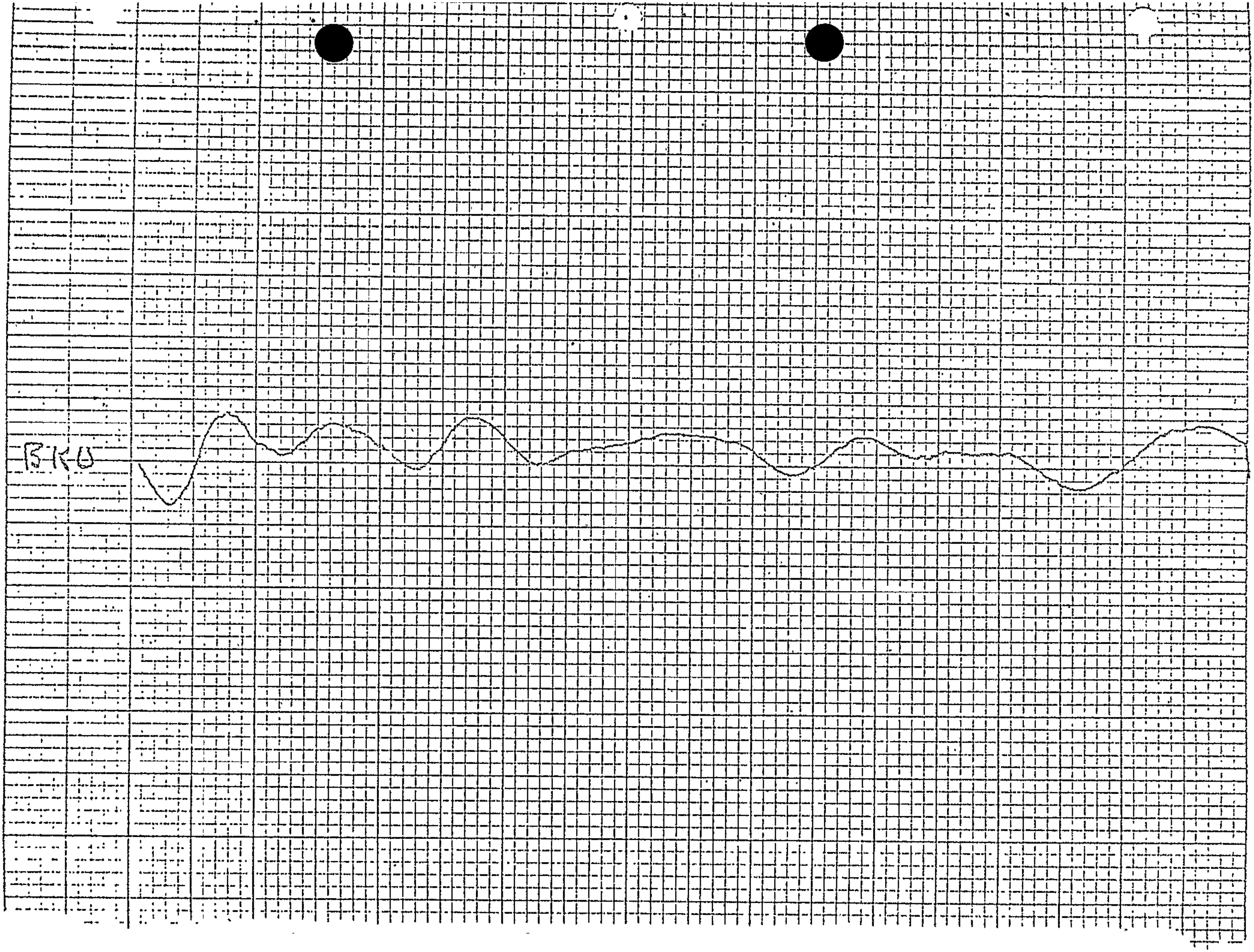
```
           5.0305E 01 2.8050E 01 4.9523E 01 6.6375E 01  7.0463E 01 1.04
           6.7726E 01 4.8705E 01 1.0726E 02 4.4760E 01  7.8320E 01 6.20
           5.9513E 01 5.2119E 01 4.7426E 01 6.2997E 01  8.0109E 01 8.35
           3.4839E 00 4.4901E 01-2.3322E 01-1.4682E 01  1.4612E 01 1.68
           8.6746E 00-5.5816E 01-5.4004E 01-2.8405E 01-2.2788E 01-4.73
          -3.7010E 01-2.9686E 01 1.7954E 01-1.1909E 01-4.4937E 01-8.74
Ψ Acme will leave the air in 10 min.......gdnite
           2.7730E 01 6.6604E 00 5.2225E 01 2.3713E 01  4.4510E 01 9.74
           3.9178E 01-1.1199E 01 2.4069E 01 1.4612E 01  2.2291E 01 2.47
           2.2042E 01 3.8538E 01 1.0381E 01 3.4947E 01  2.0371E 01 1.87
          -8.0703E 00 1.6425E 01 2.5775E 01 1.2052E 01  2.1829E 01 5.35
           1.4825E 01 4.6075E 01 4.5577E 01 4.4404E 01  4.4440E 01 2.80
           1.1910E 01 1.5323E 01 2.0869E 01 1.3581E 01-1.1625E 01-2.77
          -2.5917E 01-3.2388E 01 8.5325E 00-2.8050E 01-2.0330E 01-2.18
           2.3038E 01 2.8192E 01 1.5927E 01 2.2646E 01  2.3500E 01 2.65
           4.3444E 01 3.6227E 01 3.3276E 01 4.3586E 01  4.0920E 01 3.97
           5.2901E 01 4.6537E 01 4.2235E 01 4.1489E 01  2.8335E 01 4.80
           3.1890E 01 2.7553E 01 1.5749E 01 5.5745E 01  7.3592E 00 6.399
           4.0422E 01 1.5774E 01 3.6263E 00-9.8833E 00  2.1686E 01 3.55
          -7.0748E 00 1.3047E 01 7.5726E 00 3.0717E 01  1.2799E 00-8.99
          -2.4460E 01-9.0657E 00-2.6521E 01-7.6792E 00-8.8167E 00 5.652
           4.0707E 01 3.9213E 01 2.9046E 01 4.4831E 01  7.3592E 01 3.359
           4.6111E 01 5.5248E 01 7.4410E 01 4.0956E 01  3.9463E 01 9.492
          -2.8690E 01-4.0742E 01 1.1377E 00-3.7045E 01-4.8848E 01-8.852
           2.5775E 01 8.8721E 00-1.0808E 01 3.0184E 01  1.4150E 01 2.47
           3.5587E 01 1.7491E 01 1.7243E 01 6.0936E 01  3.6156E 01 4.547
           4.2840E 01 4.4191E 01-1.9766E 01 3.3667E 01  9.5273E 00-2.93
          -5.6455E 01-4.1953E 00-9.6343E 00-6.7903E 00-1.5821E 01-2.13
           2.7588E 01 3.3703E 01 7.6438E 00 6.1326E 01  6.9255E 01 4.38
           2.9116E 01 7.4609E-01-2.1758E 01-3.1463E 01  2.7908E 01-8.539
          -1.0026E 02-1.1739E 02-9.4816E 01-6.0015E 01-6.7477E 01-7.007
```

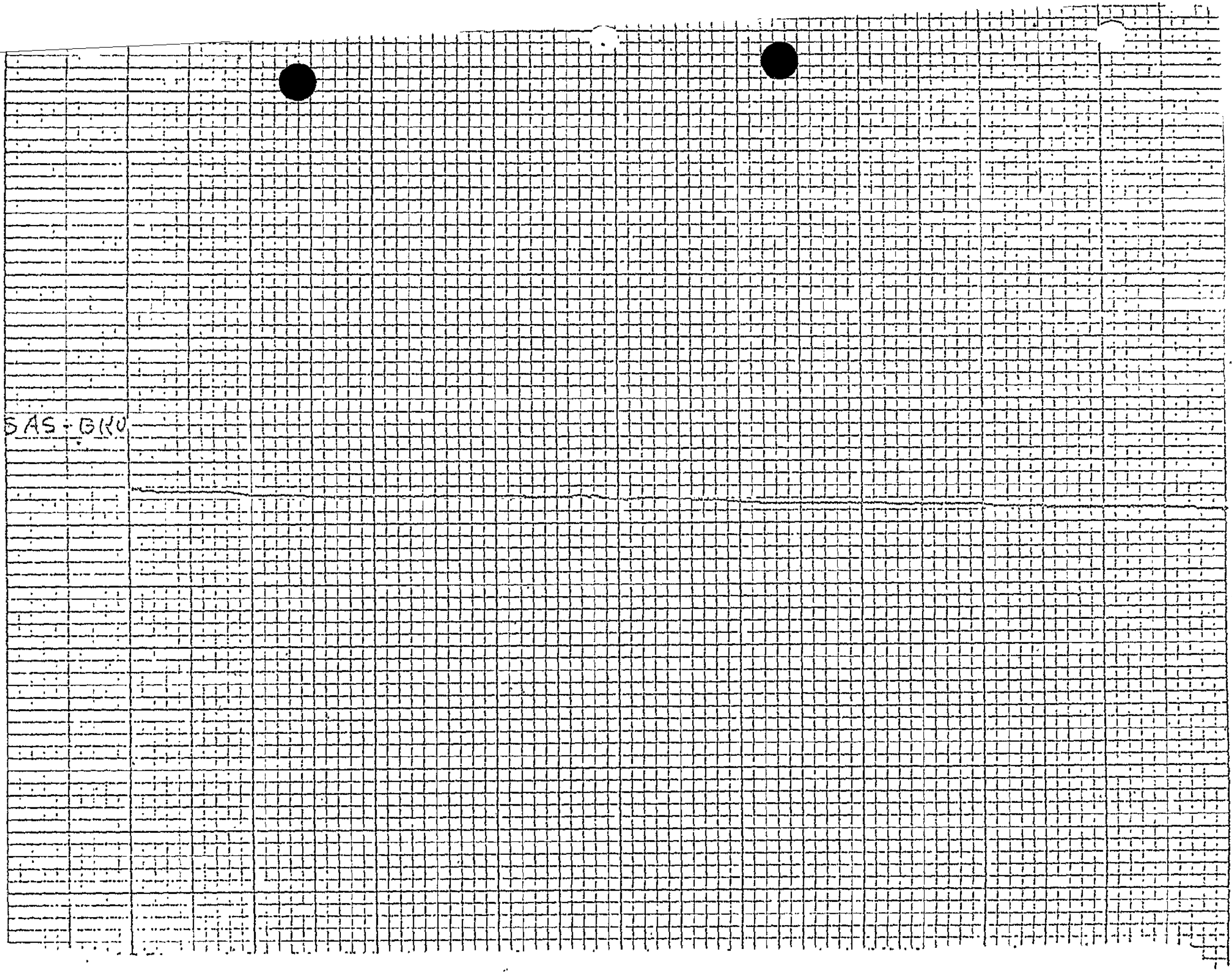
FOLDOUT FRAME

```
 7.0463E 01 1.0427E 02 1.6496E 01 1.1497E 02 7.7545E 01 1.0310E 02
 7.8320E 01 6.2002E 01 7.3983E 01 6.1201E 01 7.7253E 01 4.1986E 01
 8.0169E 01 8.3511E 01 3.8005E 01 2.5589E 01 1.0914E 01 1.7420E 01
 1.4612E 01 1.6816E 01-1.2869E 01-7.5366E 00-1.9056E 01-4.9062E 00
-2.2788E 01-4.7355E 01-6.4988E 01-1.3900E 01-2.8370E 01 6.1855E 00
-4.4937E 01-8.7461E 00 4.8000E 00 2.8086E 00-1.1021E 00 2.8394E-01

 4.4510E 01 9.7422E 00 5.0483E 01 4.7285E 00 6.6484E 00 2.6024E 01
 2.2291E 01 2.4708E 01 4.4261E 01 3.1605E 01 2.1331E 00 5.1550E 00
 2.0371E 01 1.8736E 01 1.8807E 01 1.1874E 01 1.5963E 01 7.2883E 00
 2.1829E 01 5.3505E 01 2.2220E 01-3.1643E 00 7.4054E 01 6.2535E 01
 4.4440E 01 2.8086E 01 4.7746E 01 5.7274E 01 2.5775E 01 4.5862E 01
-1.1625E 01-2.7728E 00-2.7019E 00-5.3378E 00-5.9370E 00-2.9507E 00
-2.0336E 01-2.1829E 01-8.6391E 00-2.9295E 01-2.1295E 01 1.0061E 01
 2.[illegible]0E 01 2.6557E 01 2.5348E 01 3.7258E 01 3.3490E 01 3.4699E 01
 4.[illegible]20E 01 3.9711E 01 3.9285E 01 5.2652E 01 3.2814E 01 5.0235E 01
 2.8335E 01 4.8066E 01 5.8411E 01 4.7924E 01 2.9935E 01 2.3855E 01
 7.3592E 00 6.3994E-01 2.1367E 01 2.2362E 01 3.5907E 01 2.5348E 01
 2.1686E 01 3.5552E 00 1.4790E 01 1.1234E 01 2.8655E 01 1.4292E 01
 1.2799E 00-8.9945E 00-1.7503E 01 4.8350E 00-2.8299E 01-4.4797E 00
-8.8167E 00 5.6528E 00 5.8303E 00-1.6353E 00 3.0894E 01 1.5536E 01
 7.3592E 01 3.3596E 01 3.5125E 01 7.2312E 01 6.1042E 01 4.9772E 01
 3.9463E 01 9.4924E 00 1.6810E 01 2.2398E 01-1.5358E 01-1.2336E 01
-4.8848E 01-8.8523E 00-2.3891E 01-2.7908E 01-4.5859E 00-5.6918E 01
 1.4150E 01 2.4780E 01-8.5325E 00 2.8193E 01 6.1326E 01 4.7213E 01
 3.6156E 01 4.5471E 01 2.2361E 01 4.4404E 01 3.0006E 01 4.6004E 01
 9.5273E 00-2.9365E 01-3.5694E 01-9.8835E 00-7.4302E 00 2.2184E 01
-1.5821E 01-2.1366E 01 3.0219E 01 5.6527E 01-1.5074E 01 2.1046E 01
 6.9255E 01 4.3870E 01 1.6197E 02 5.7523E 01 7.9630E 01 2.7695E 01
 2.7908E 01-8.5395E 01-5.5731E 01-2.6592E 01-1.0217E 02-9.0728E 01
-6.7477E 01-7.0072E 01-8.8879E 01-6.4668E 01-2.5455E 01-3.0503E 01
```

FOLDOUT FRAME 2


BKU


SAS-GRU

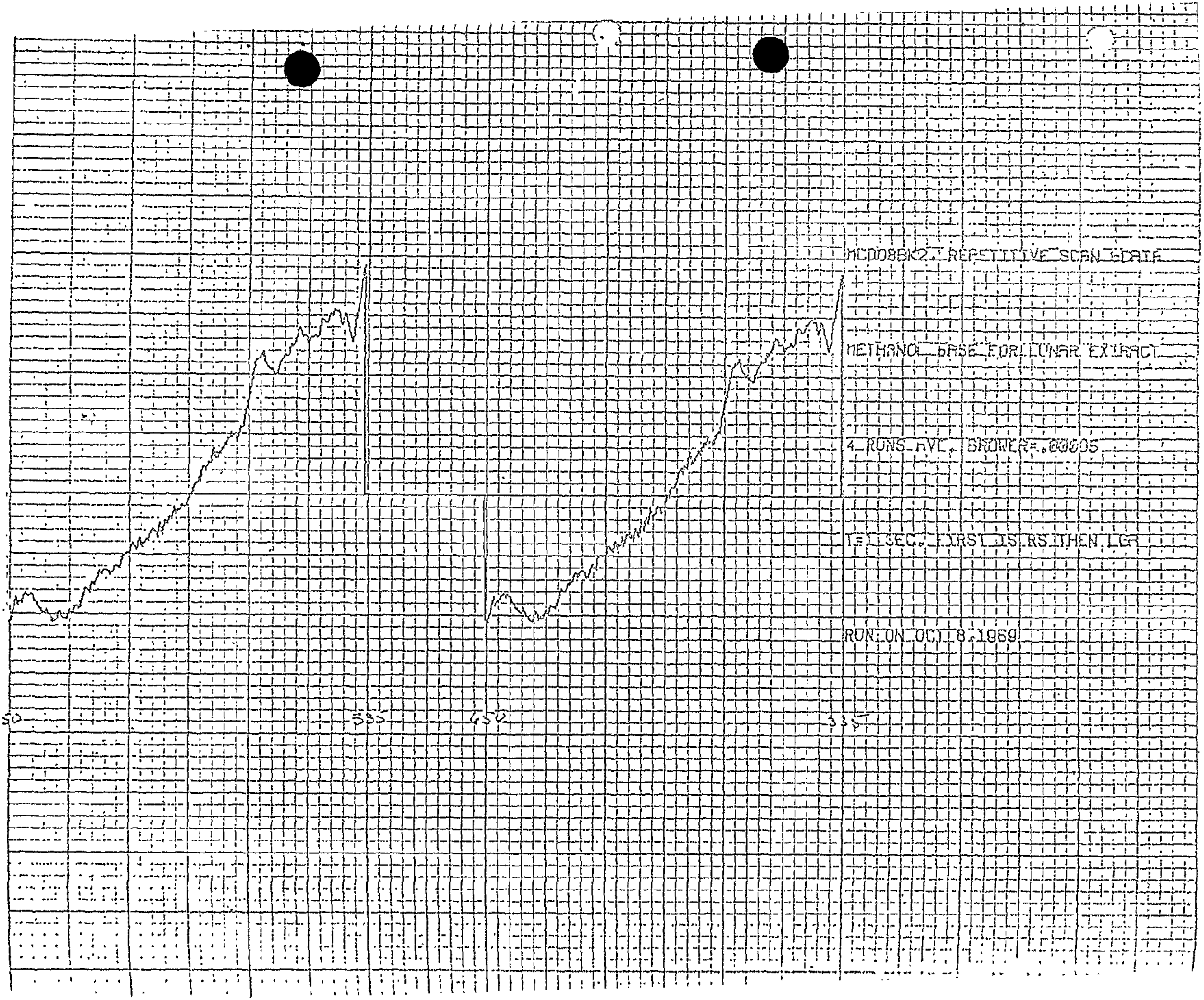
Appendix B

The digital recorded values obtained during the sand blank measurement are not included in this report. They are, however, on permanent computer file:

Sand sample	SANDBLNK
Background (MeOH)	LUN09_BK

Appendix C

Additional data obtained is graphically presented in this section. Each run may be reconstructed from the division of the integrated signal divided by the integration time and from the X1 analog channel directly. In the dual plots the data from the two channels are separated by a one inch zero level. The horizontal scale is from the 650 dial reading to the 335 dial reading. Wavelength is equal to the dial reading plus 10. The vertical scale of the dual plots is different from that used in the body of the report. Unless otherwise noted, one inch corresponds to 0.000025 delta A. Appropriate comments have been included before each set of curves.



MCD08BK2. REPETITIVE SCAN DATA

METHANOL BASE FOR LUNAR EXTRACT

4 RUNS AVE. BROWER=.00005

T=1 SEC. FIRST IS RS THEN LGR

RUN ON OCT 8,1969

Fig. 6a

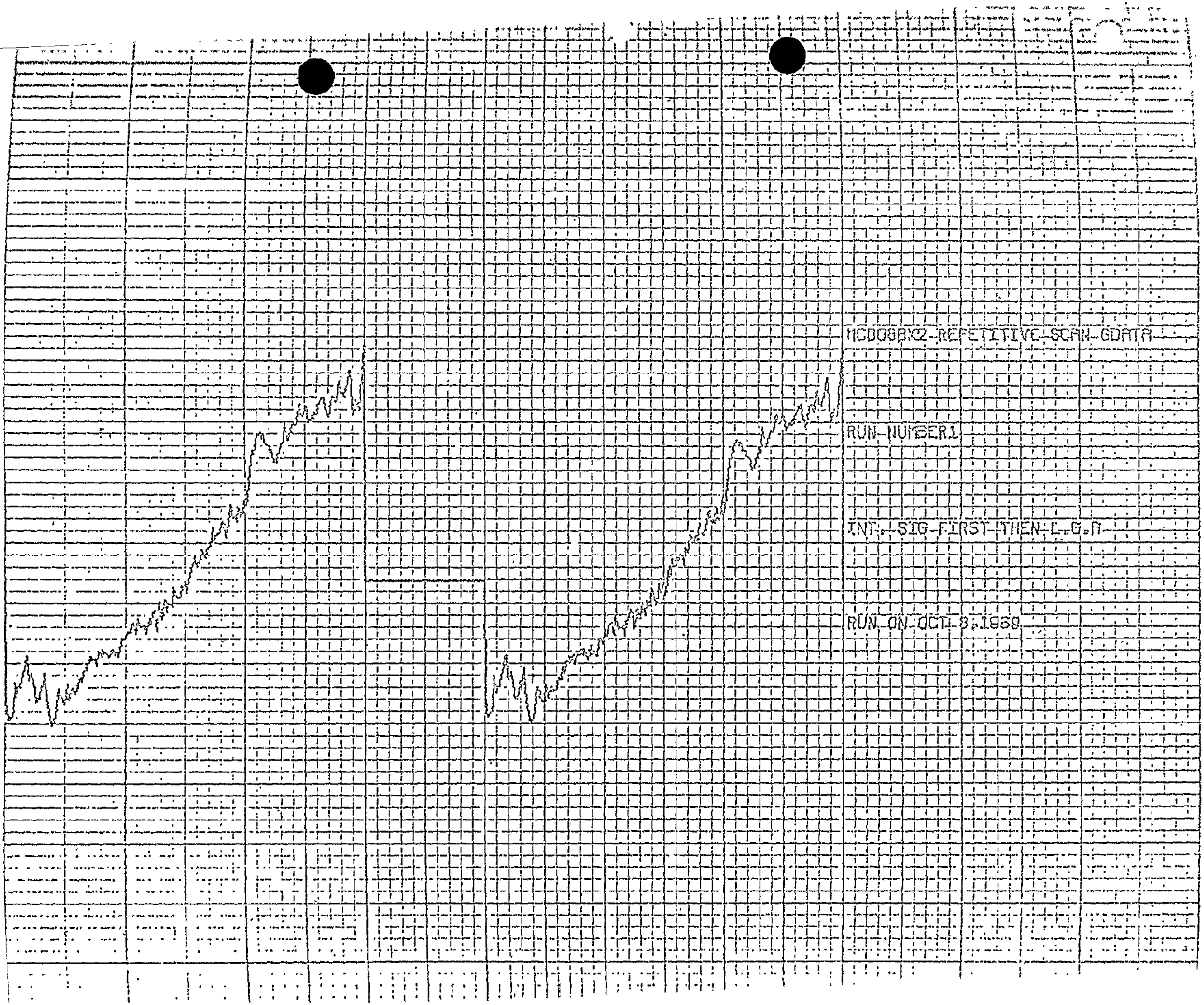

MCDOSB:X2 REPETITIVE SCAN GDATA
RUN NUMBER1
INT. SIG FIRST THEN L.G.A
RUN ON OCT 8,1968

FIG. C16

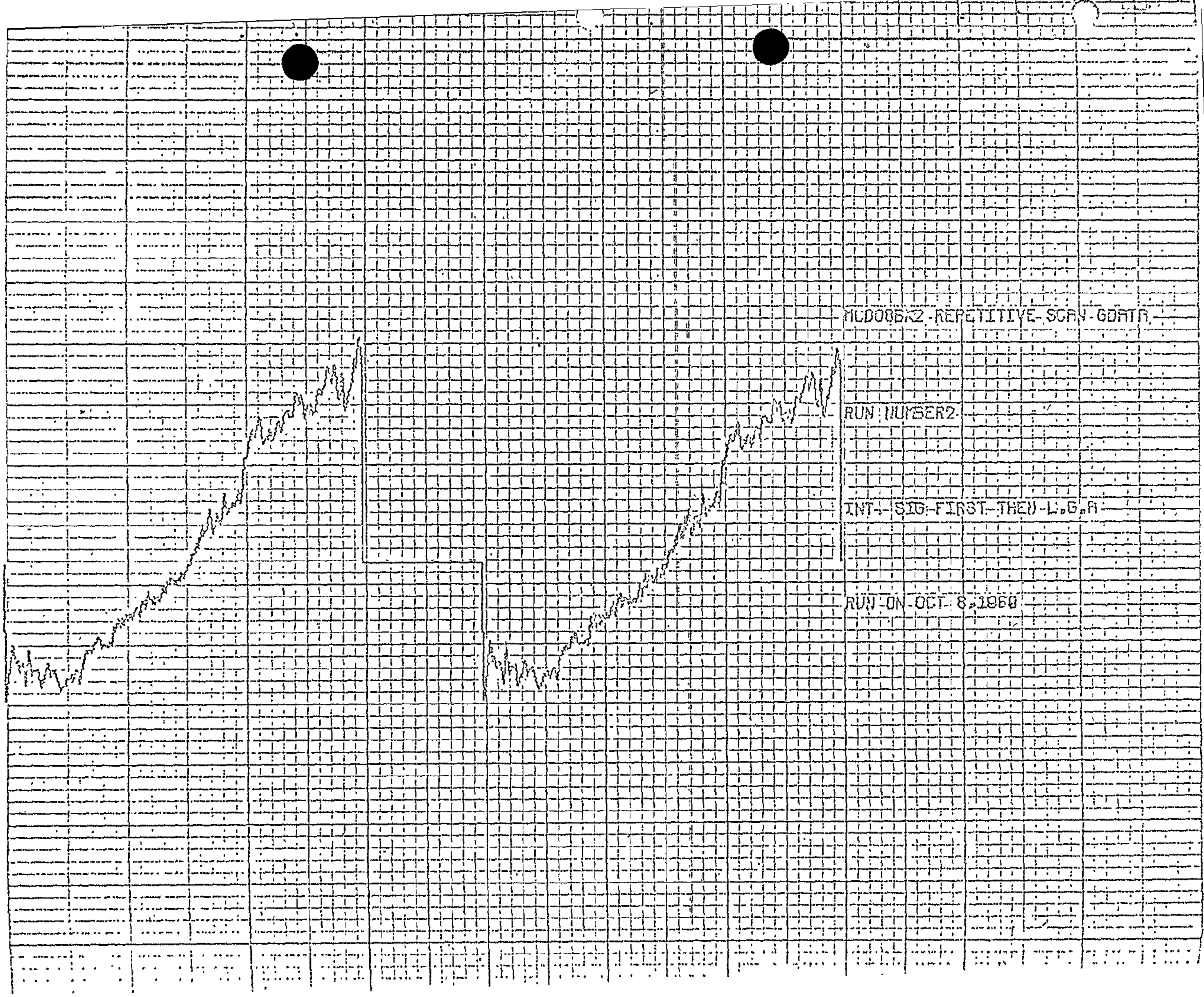

MCD008K2 REPETITIVE SCAN GDATA
RUN NUMBER2
INT.- SIG FIRST THEN L.G.A
RUN ON OCT 8,1980

Fig. C-2

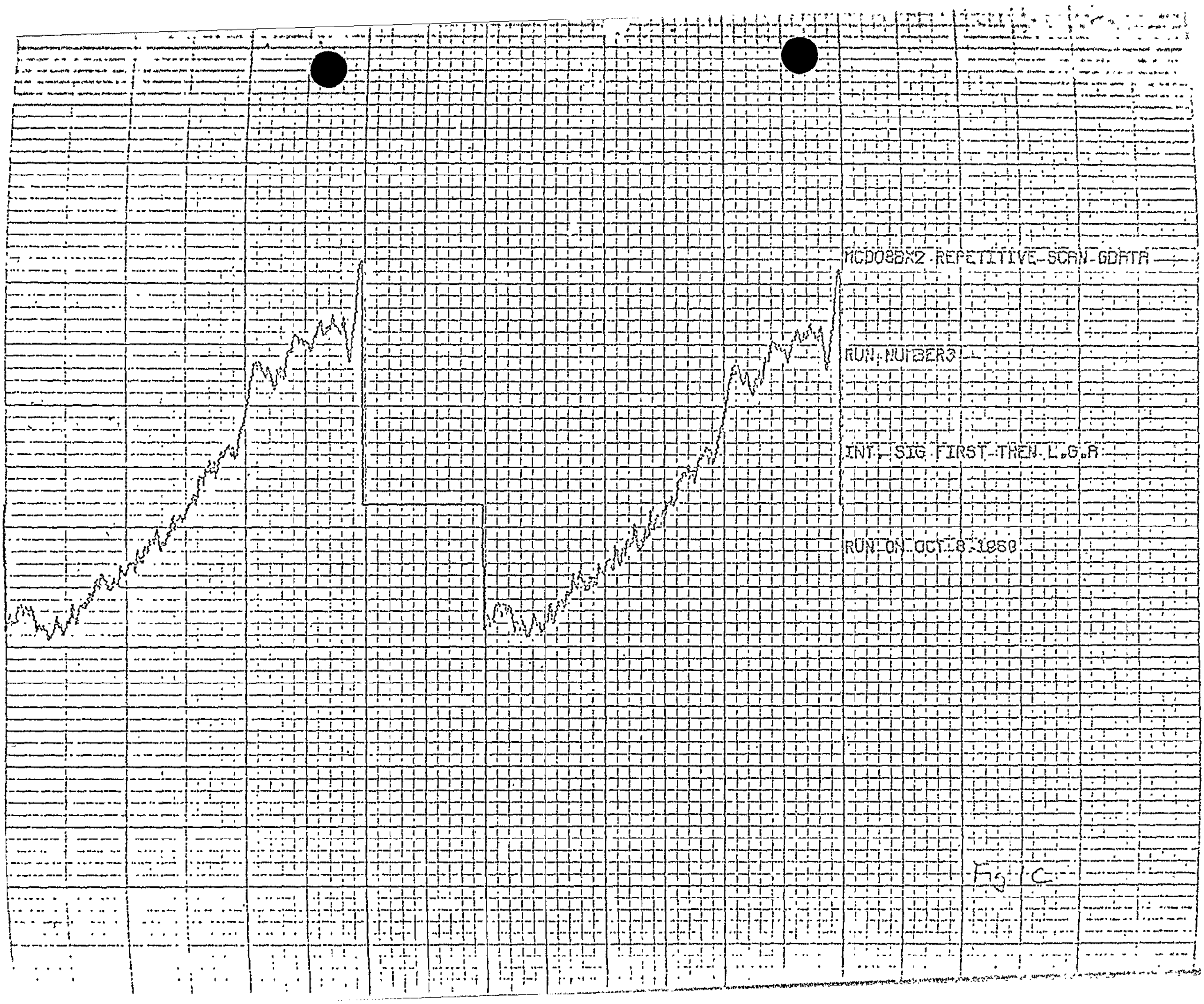


Fig 1C

Fig. C1d

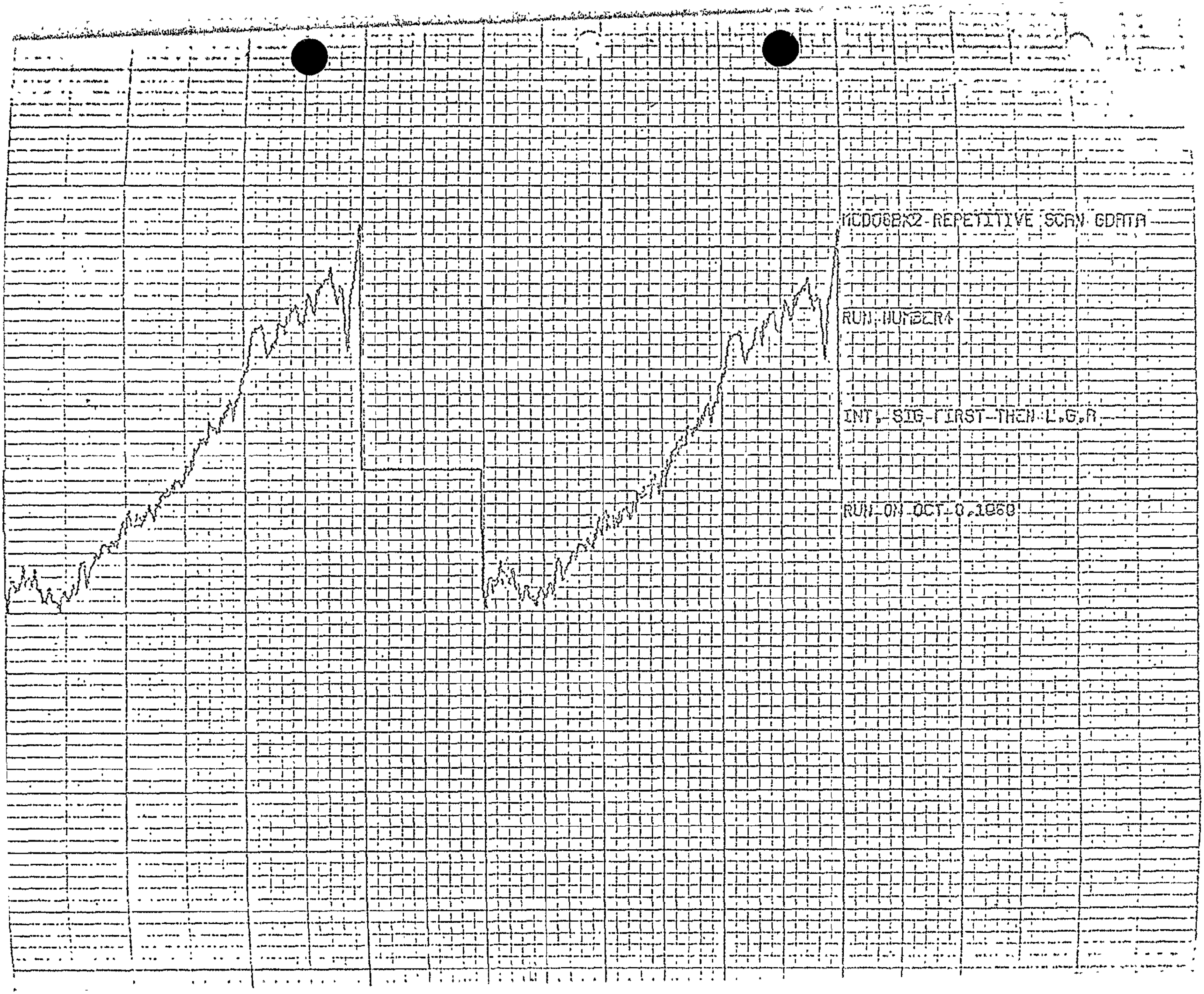
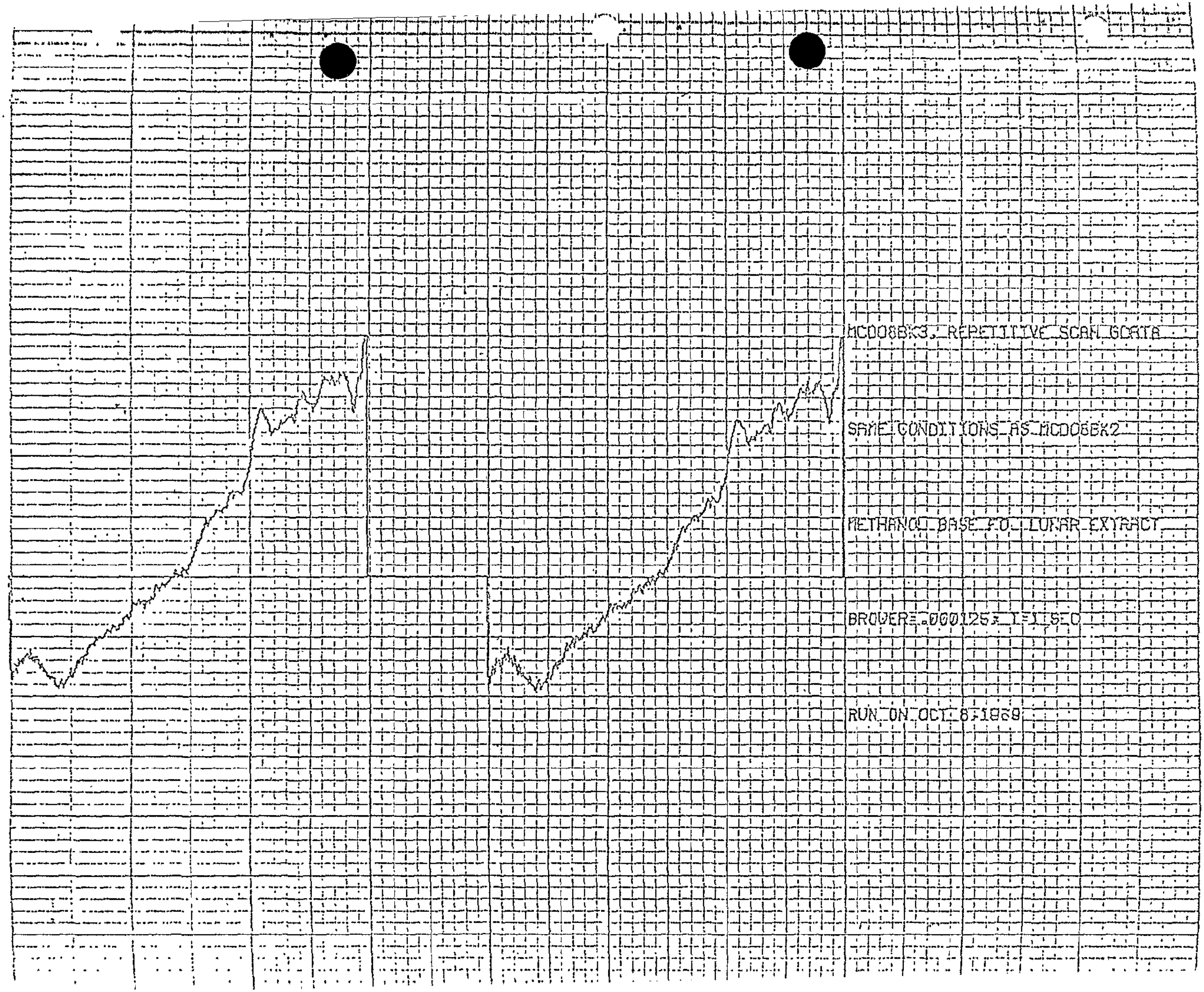

MCD06BX2-REPETITIVE SCAN GDATA
RUN NUMBER4
INT. SIG FIRST THEN L.G.A
RUN ON OCT 8,1980

Fig C1d

Figures Cla through Cle are four runs made during the morning of 8 October with background of methanol. The sample cell leaked and later ACME crashed. However the four runs look all right. Figure Cla is the average (sum and divide by 4) of the four runs. This set of data has not been used because of the leaking cell. However, note the Brower setting of this set and the next set. The Brower was at different settings, but the signal and the plot were and are essentially the same.

Figure C2a is the sum of 2b through 2e. This was the second run on methanol background. This time the sample cell held the fluid with no apparent leaks

These, and all other runs not designated TREAK, were taken in the primary mode: One cycle of data recorded by the computer and the wave length advanced 1.05 dial reading.



MCD08BK3, REPETITIVE SCAN GDATA

SAME CONDITIONS AS MCD08BK2

METHANOL BASE FO. LUNAR EXTRACT

BROVER= .000125, T=1 SEC

RUN ON OCT 8, 1969

Fig C2a

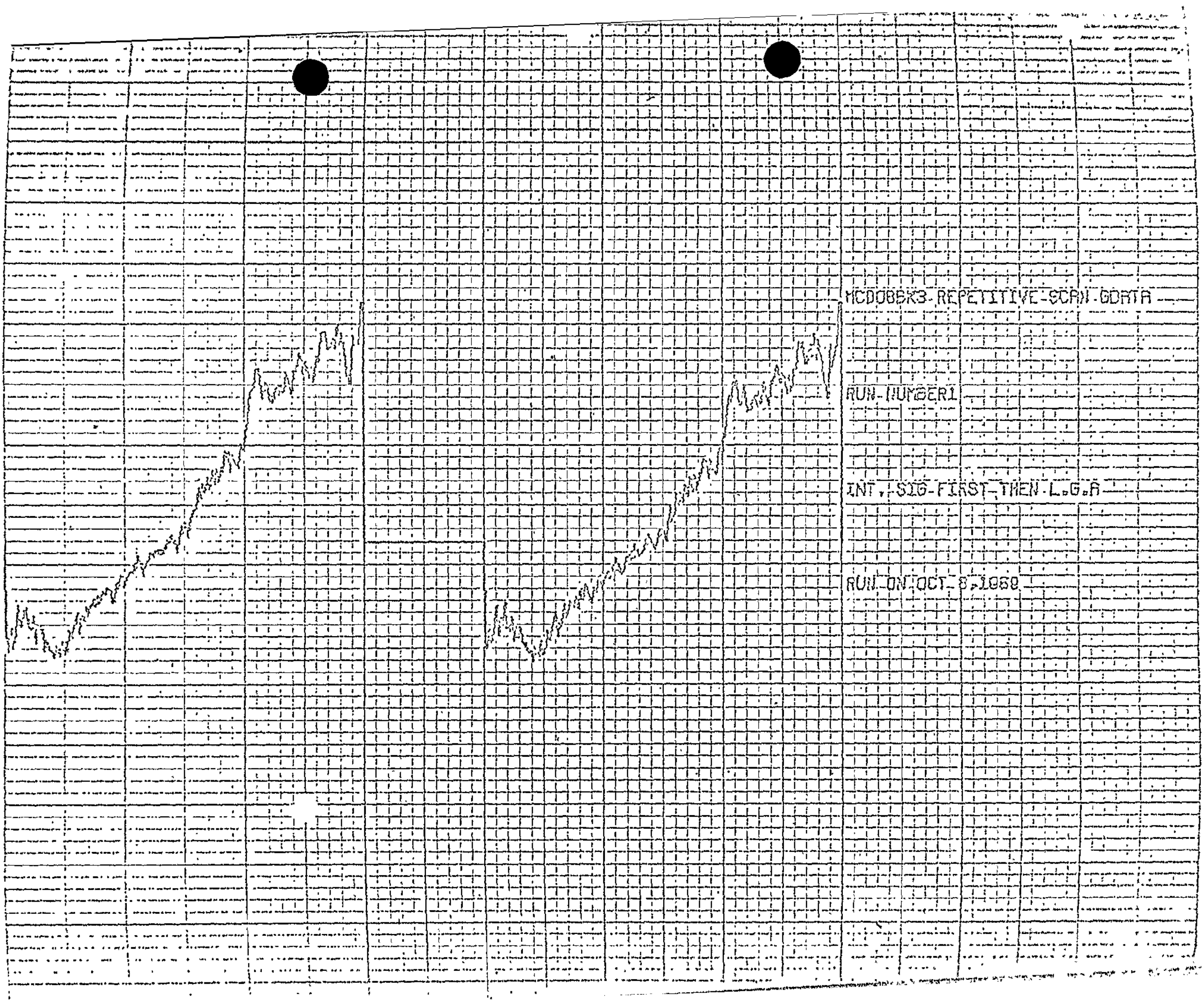

MCDOBBX3 REPETITIVE SCAN GDATA
RUN NUMBER1
INT. SIG FIRST THEN L.G.A
RUN ON OCT 8,1980

Fig C2b

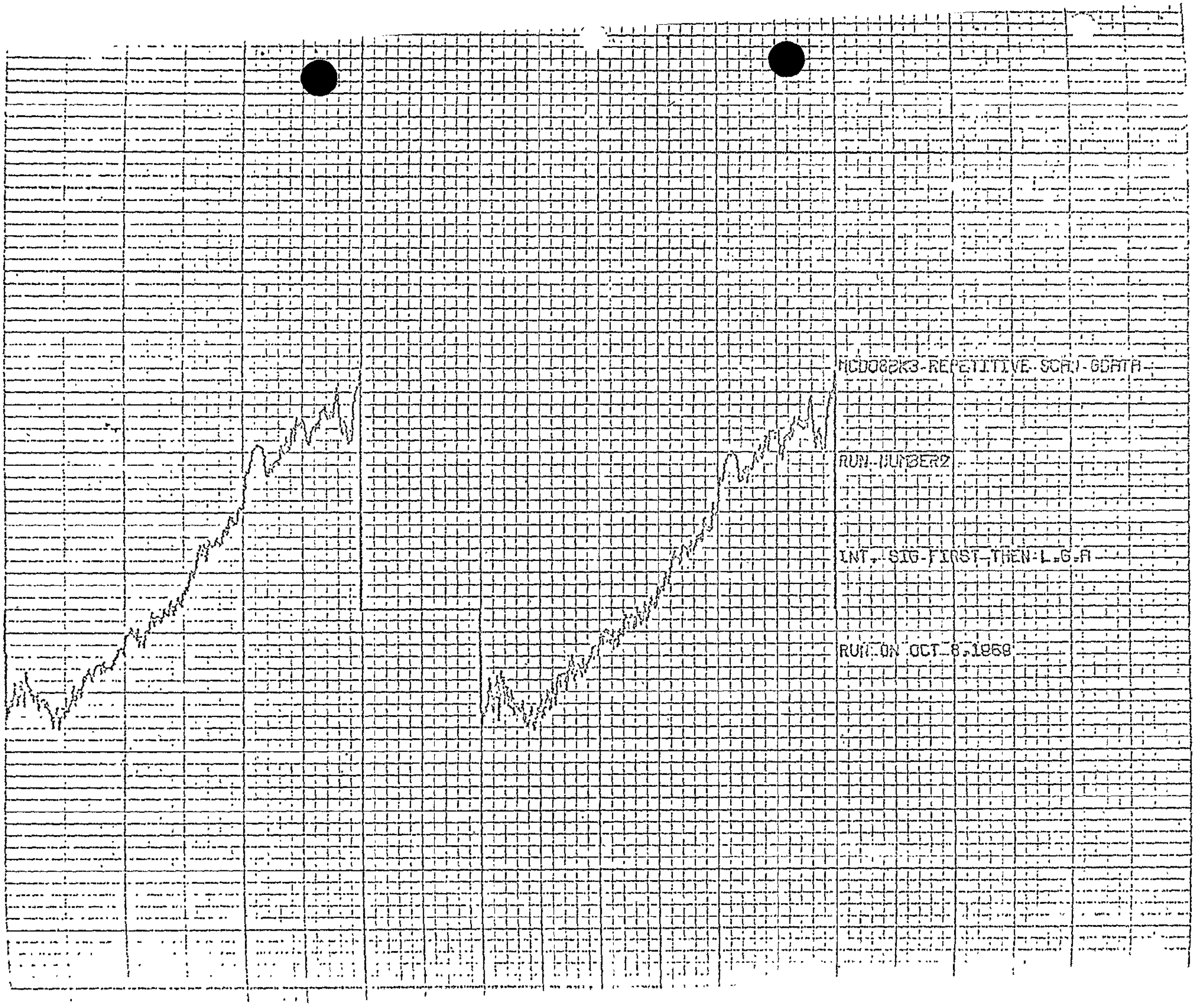

MCD082K3-REPETITIVE SCAN-GDATA
RUN-NUMBER2
INT. SIG FIRST THEN L.G.A
RUN ON OCT 8,1969

Fig C2e

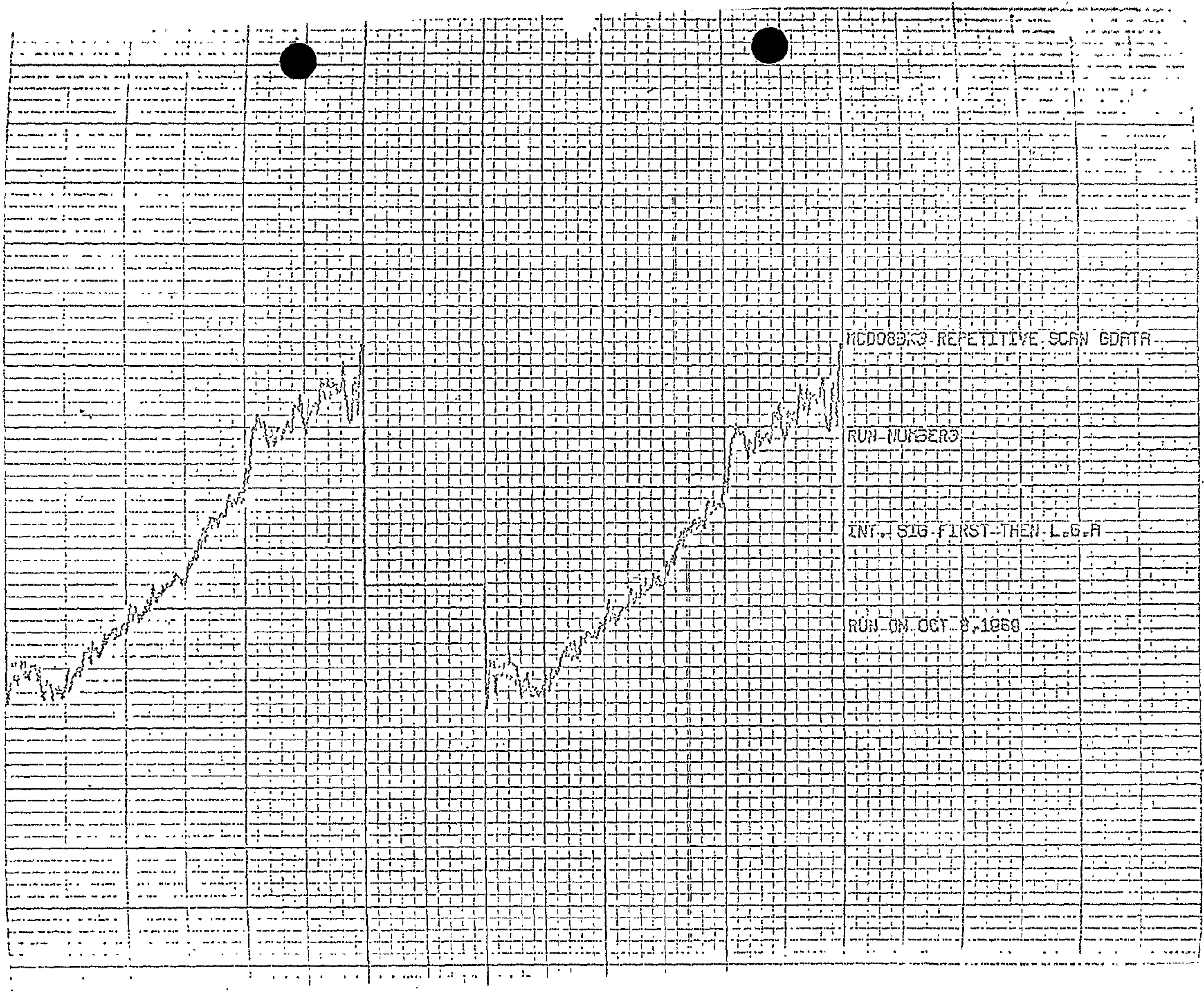

MCD08DK3 REPETITIVE SCAN GDATA
RUN NUMBER3
INT. SIG FIRST THEN L.G.A
RUN ON OCT 8,1968

Fig C2d

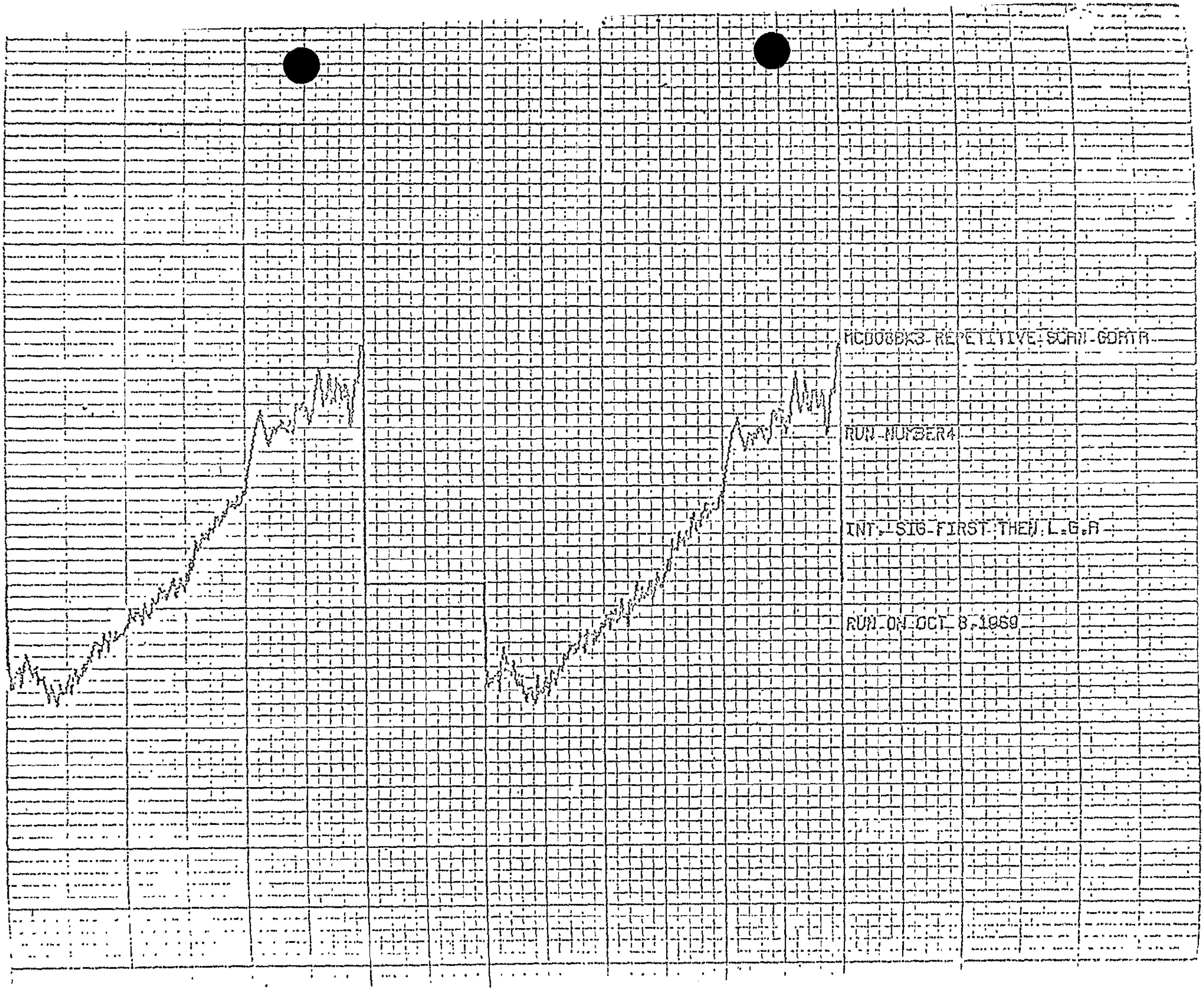

MCD08BX3 REPETITIVE SCAN GDATA
RUN NUMBER4
INT. SIG FIRST THEN L.G.A
RUN ON OCT 8,1969

Fig C2e

The figures are from the first runs on the lunar extract. Figure C3 is the averaged sum of C3a through C3h. A check of the consistence of the runs is made in Figure C4A and C4B. In one case the first four runs of set C3 were subtraced from the last four runs. The difference and the smoothed difference are plotted. In Figure C4A the scale is given in delta A. Then the odd runs were subtracted from the even runs. The results are in other set of difference and smoothed differences. These and their comparisons are a measure of the consistency of this type of data acquisition.

The average of set C2 (background) is subtracted from the average of set C3 (lunar sample). The result is shown in Figure C5 and Figure C6.

Figure C5 is the difference, and hence the assumed signal from the lunar sample. This has been derived from the integrated channel. Figure C6 is similar, but from the analog channel. These figures should be compared with SAS and BKU of the Oct. 9 report. Figure C5 and C6 represent the second reduced values of the lunar runs. The delta A scale is consistent, 0.00001/per inch, as read on the Brower.

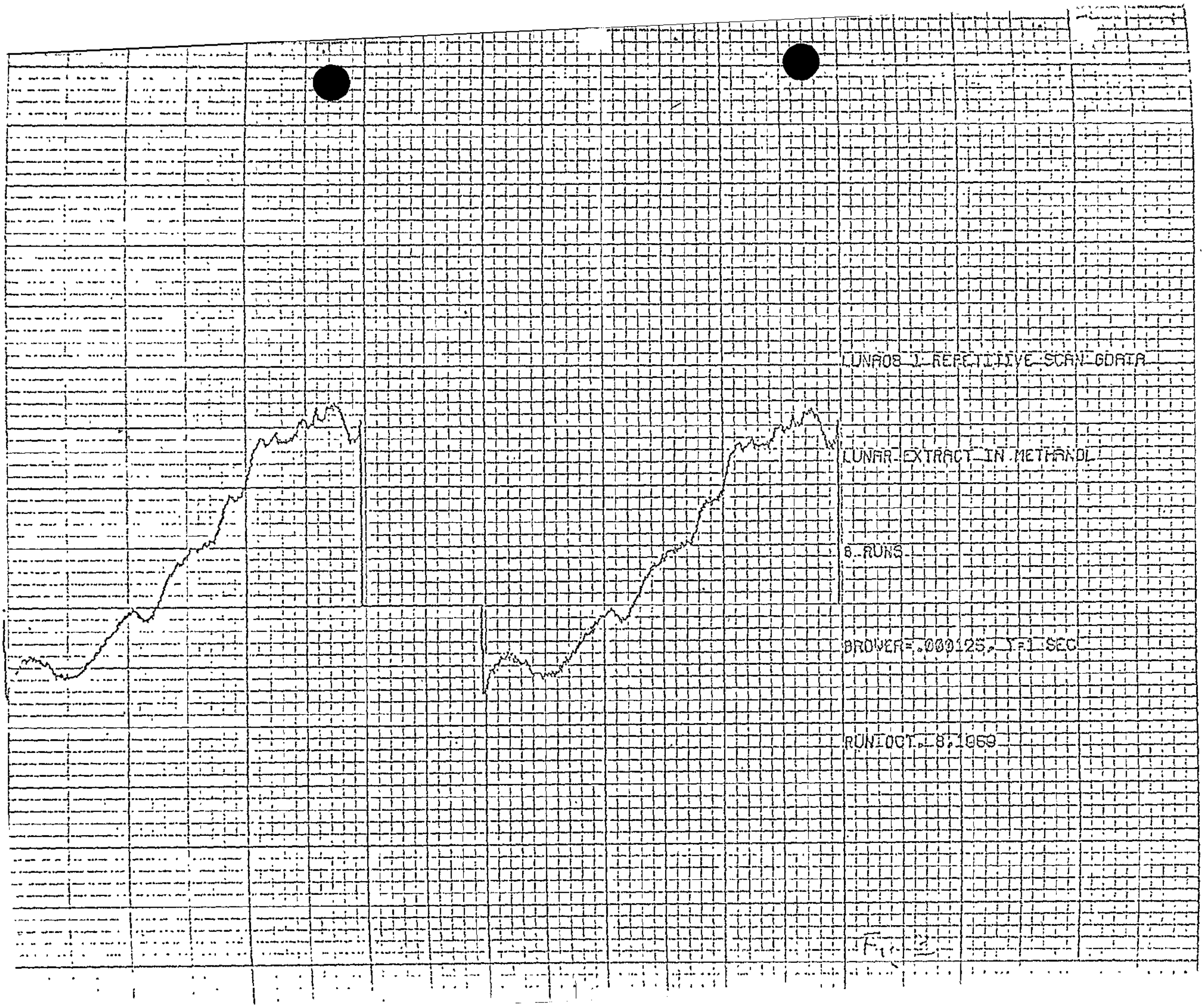

LUNA08 1 REPETITIVE SCAN GDATA
LUNAR EXTRACT IN METHANOL
8 RUNS
BRDVER=.000125, T=1 SEC
RUN OCT. 8,1969

Fig. 2

FIG C3

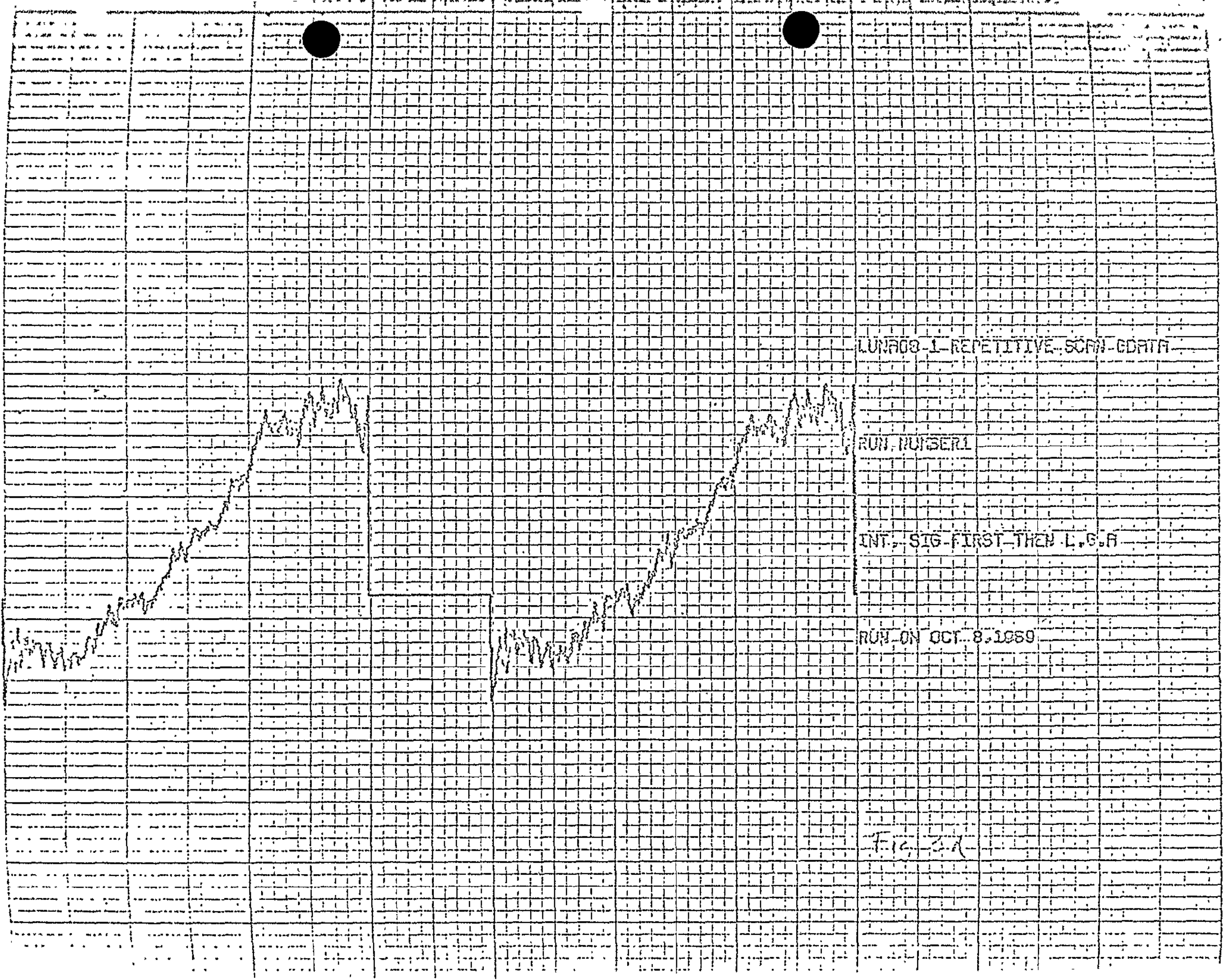

LUNA03-1 REPETITIVE SCAN GDATA
RUN NUMBER1
INT. SIG FIRST THEN L.G.A
RUN ON OCT 8,1969

Fig. 2a

Fig. 2a

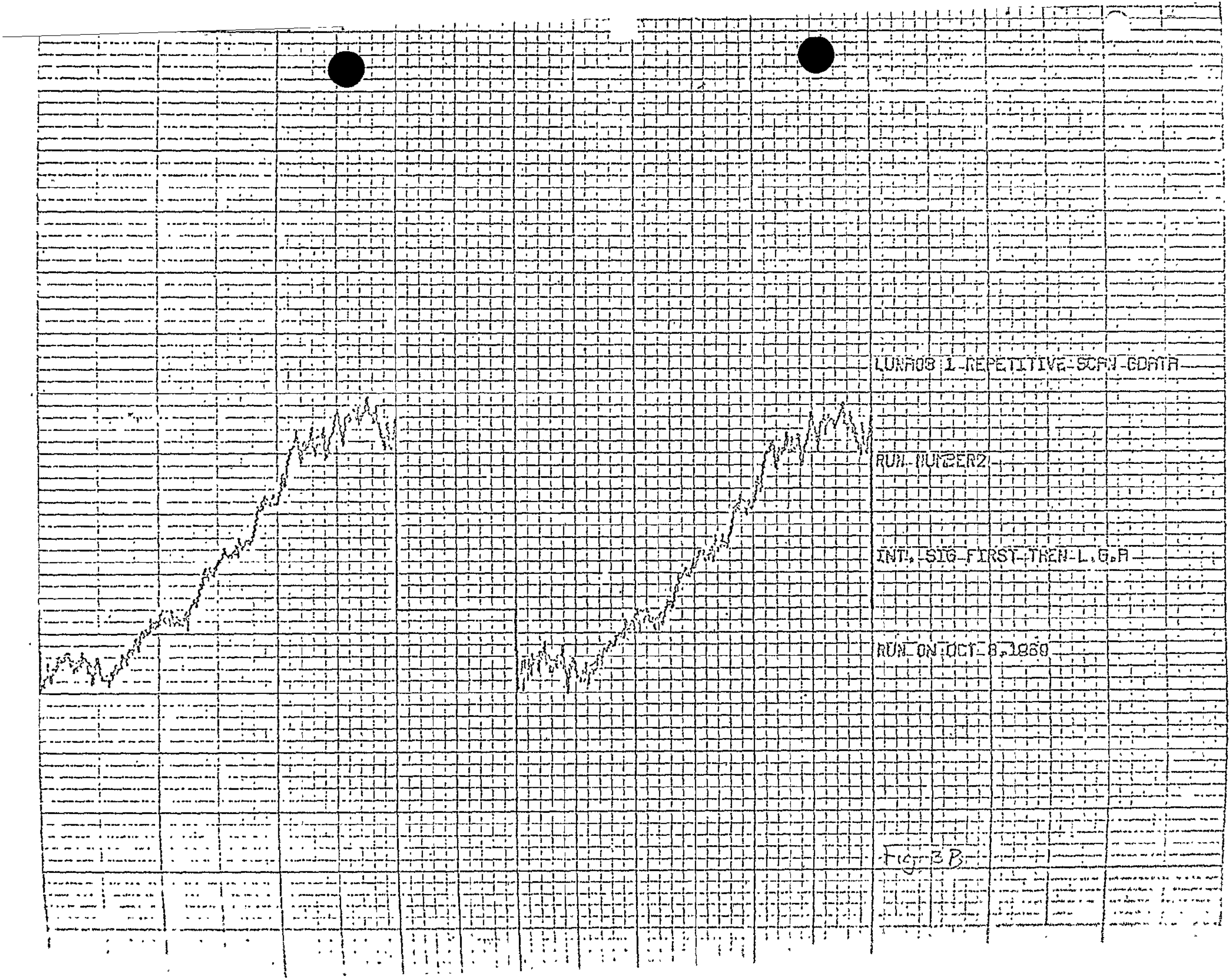


Fig 3B

Fig C36

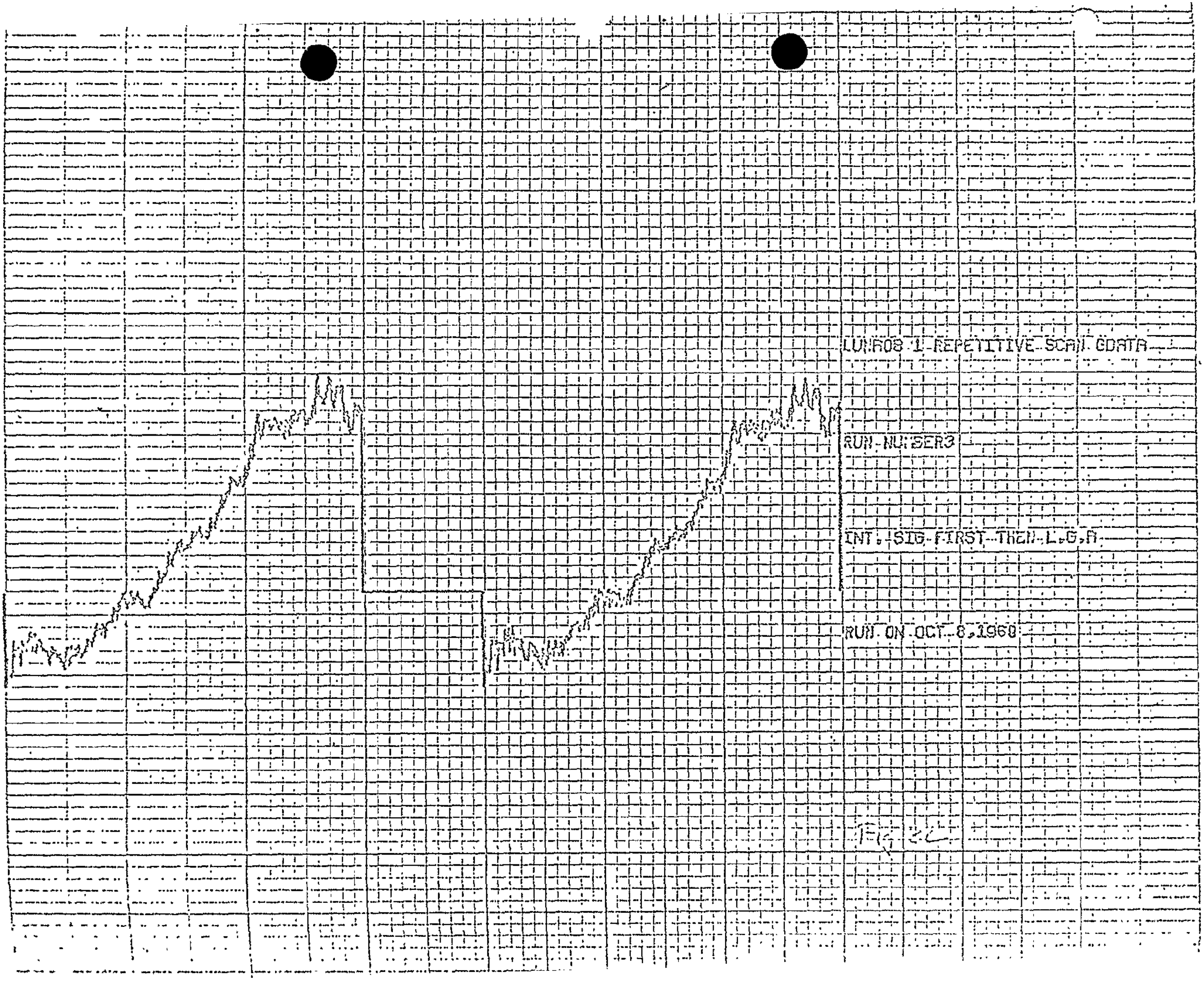


Fig 2C

Fig C3c

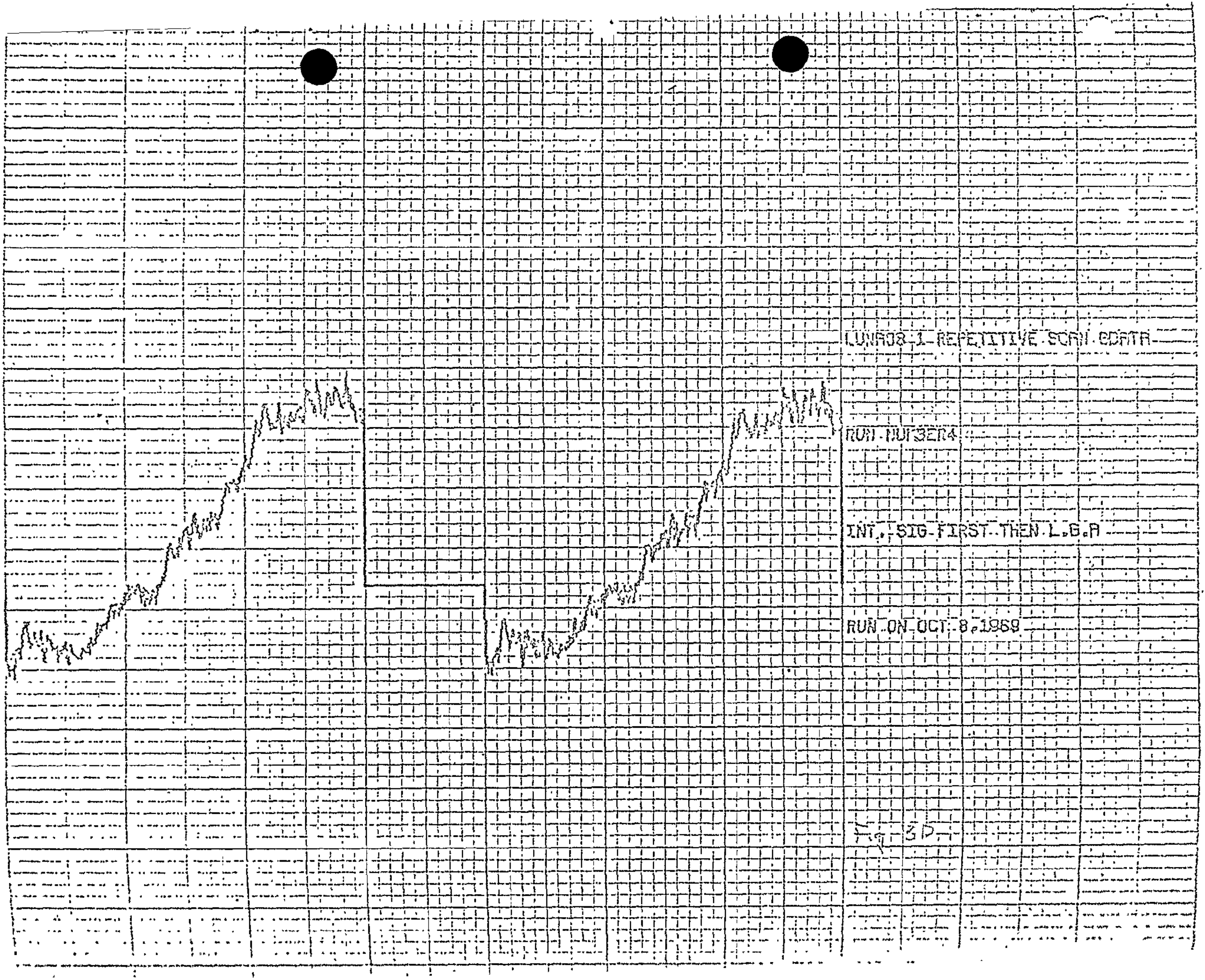


Fig 3D

Fig C3d

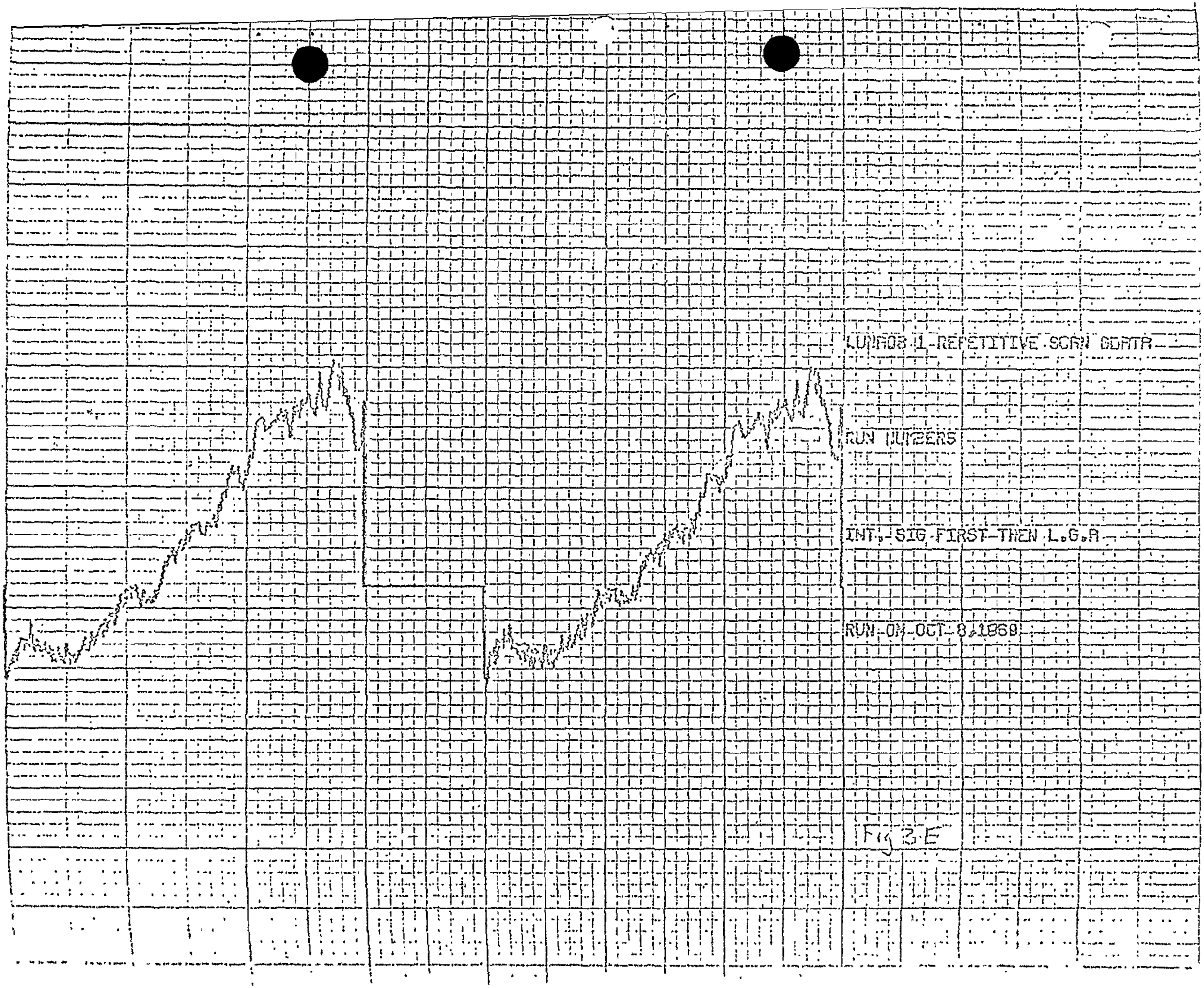


Fig 3E

Fig. C3e

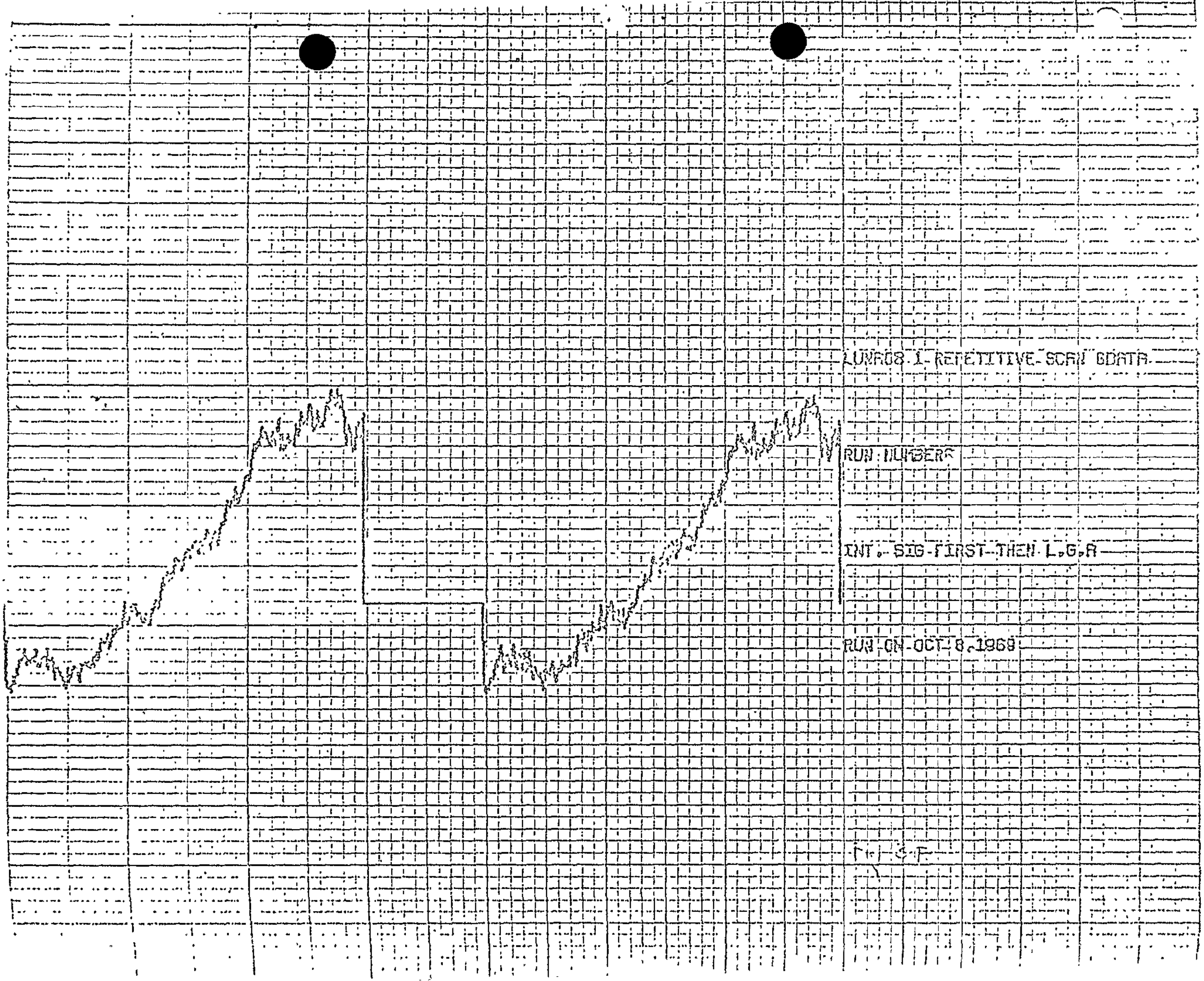

LUNA08.1 REPETITIVE SCAN 6DATA
RUN NUMBERS
INT. SIG FIRST THEN L.G.A
RUN ON OCT 8,1969
Fig 3F

Fig C3f.

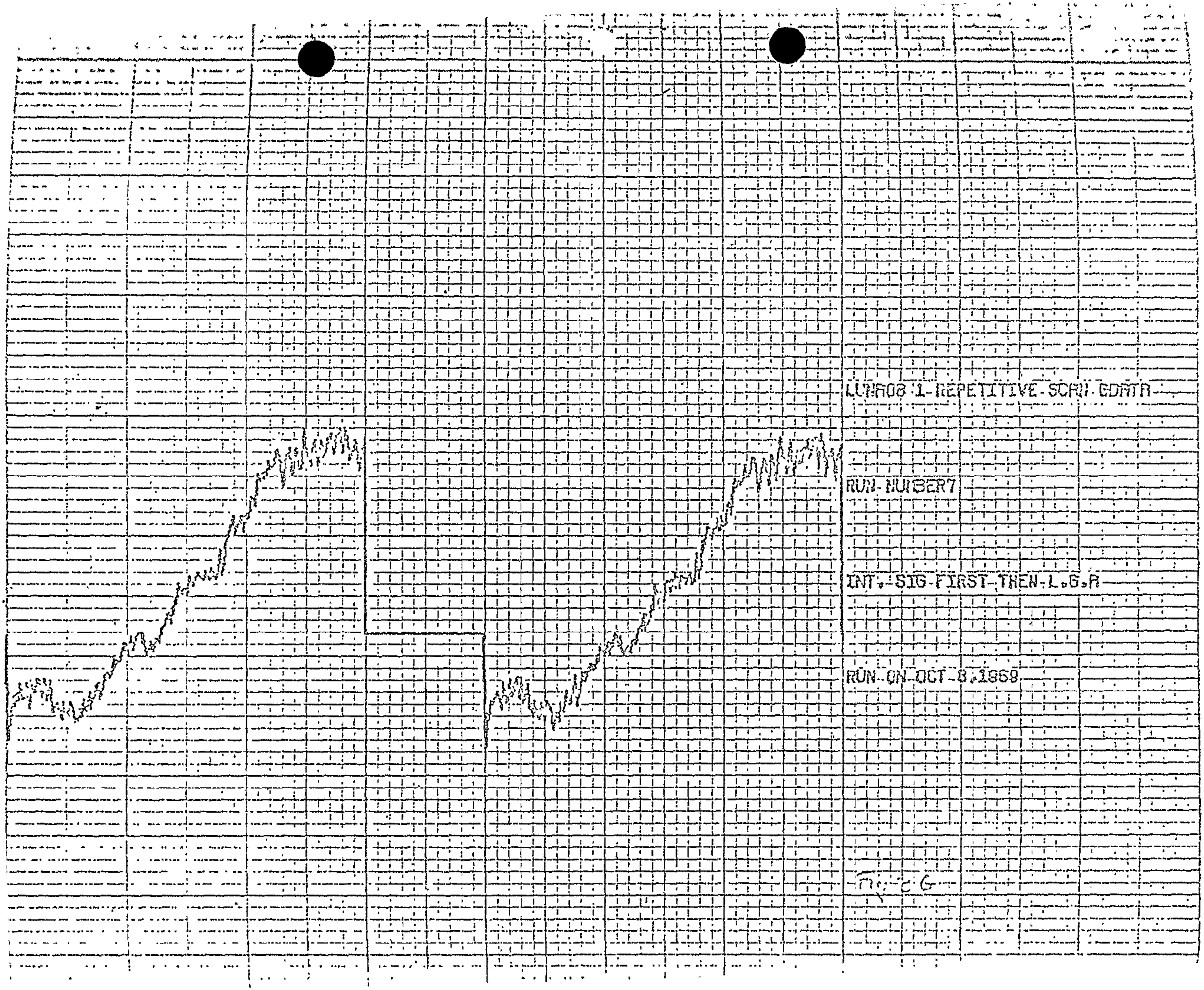

LUNA08 1-REPETITIVE-SCAN-EDATA
RUN-NUMBER7
INT.-SIG-FIRST-THEN-L.G.R
RUN-ON-OCT-8,1969
Fig C6

Fig C3g.

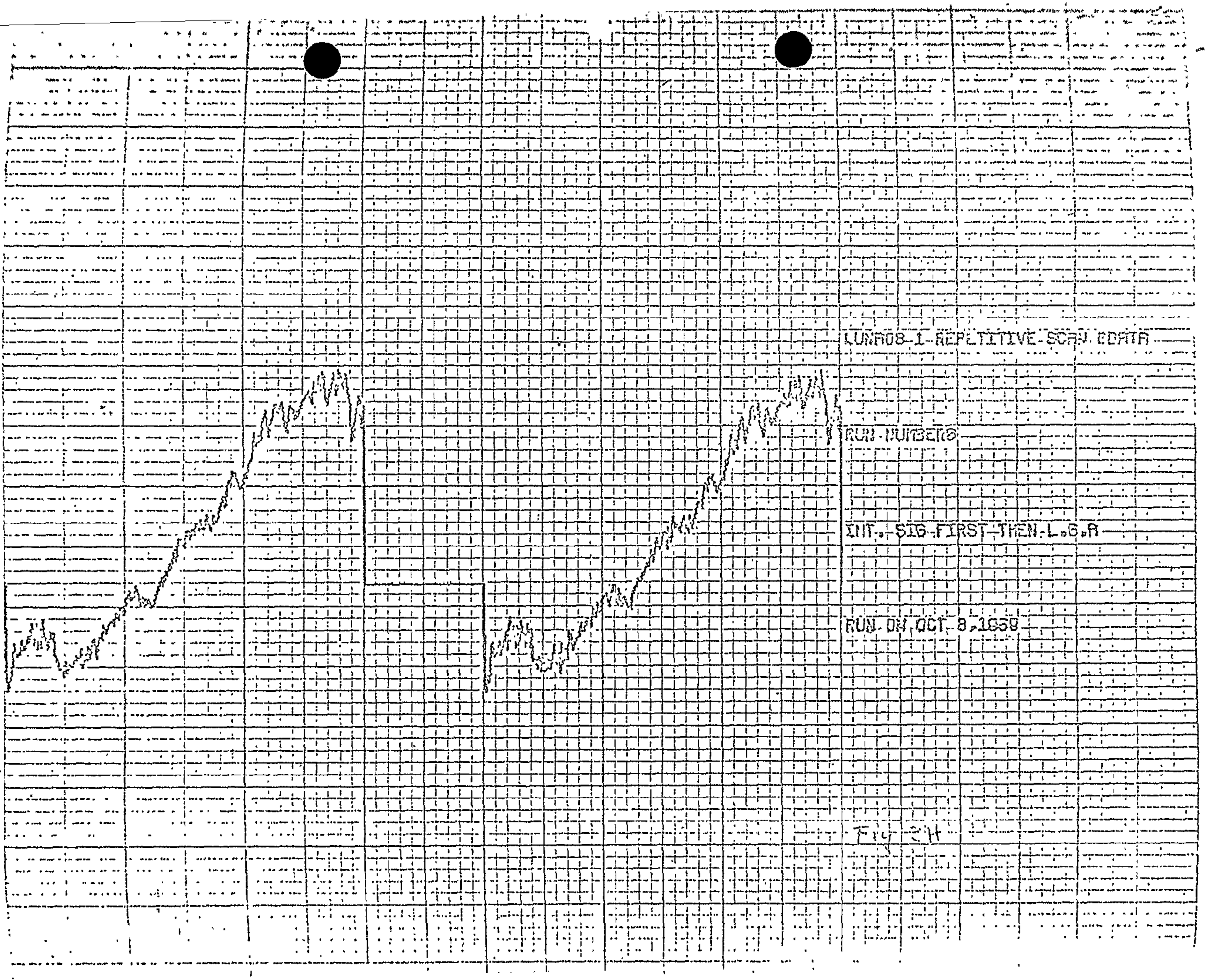


Fig 2H

Fig C3h

FIG C4a

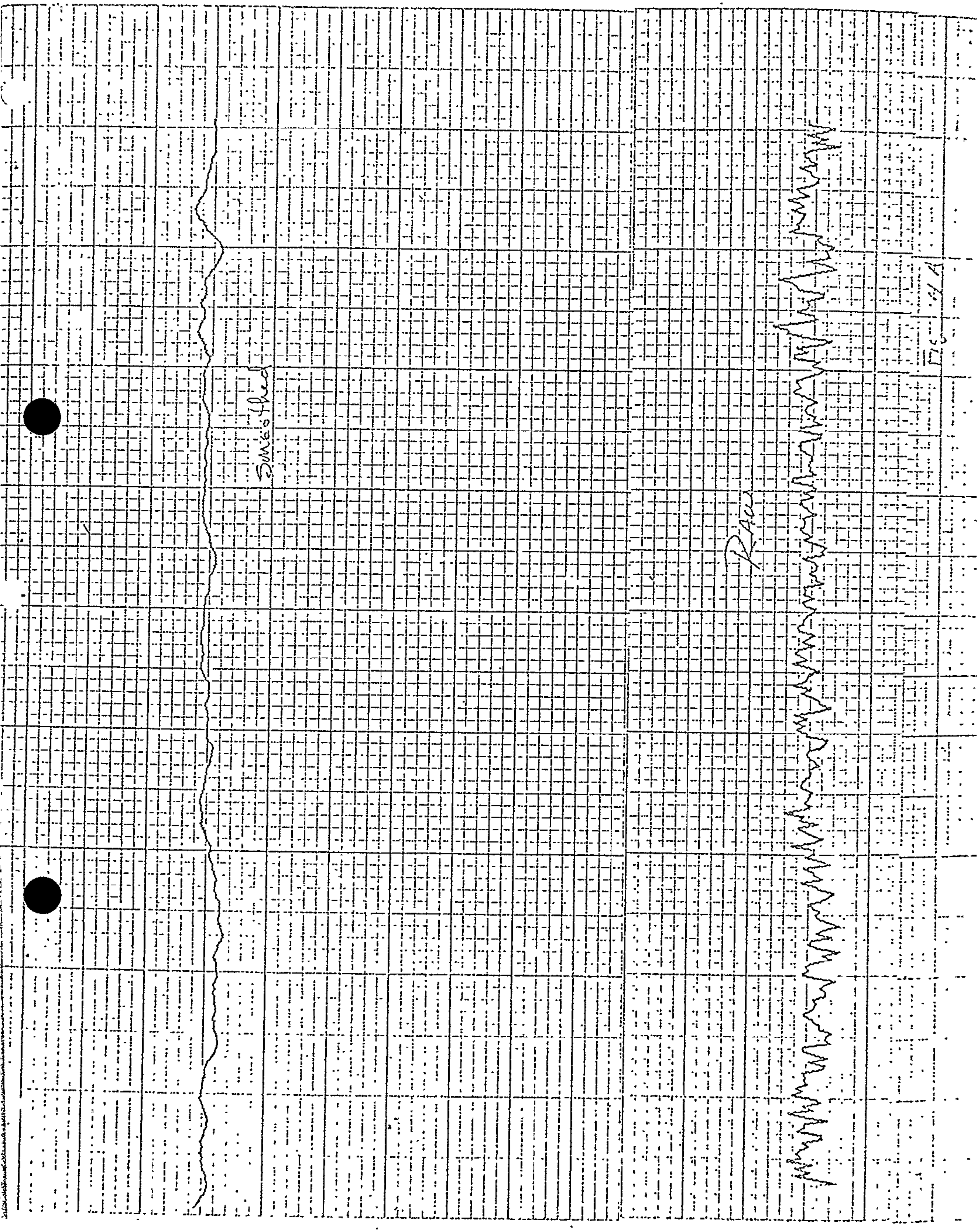


FIG. 4A

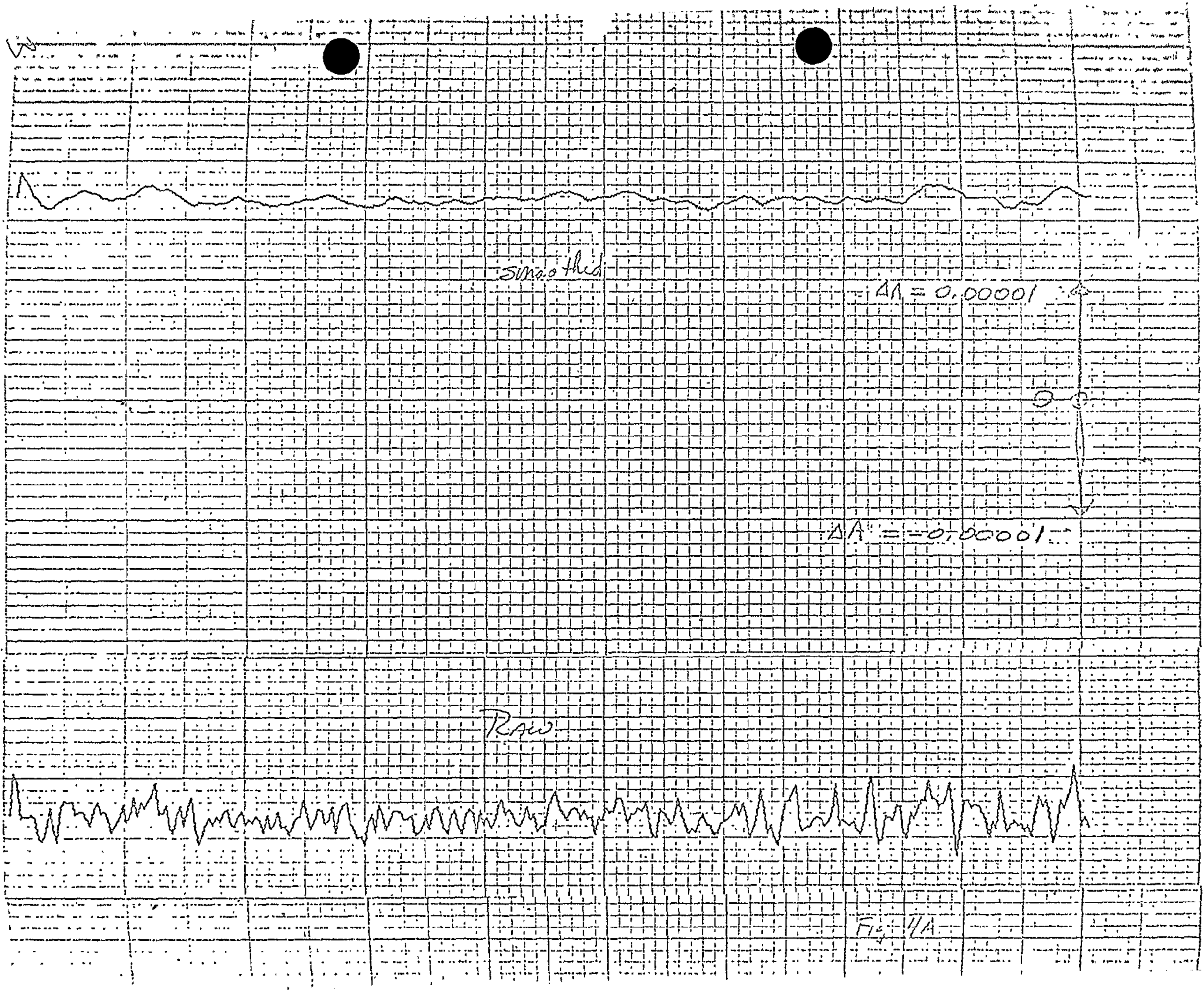


Fig 11A

Fig C4b

(2,4,6,8) - (1,1,1,

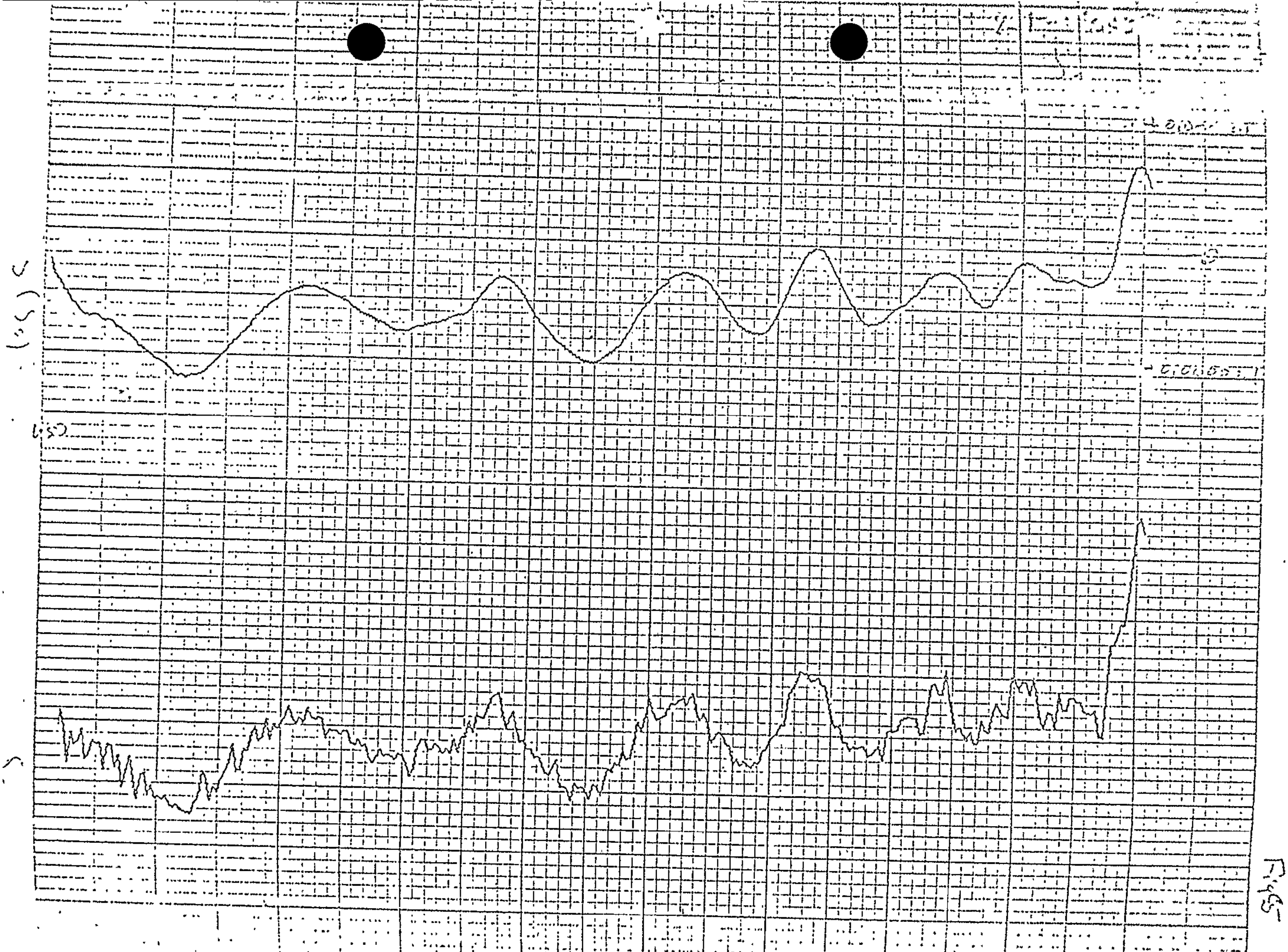


Fig 5

Fig5

Fig 6a

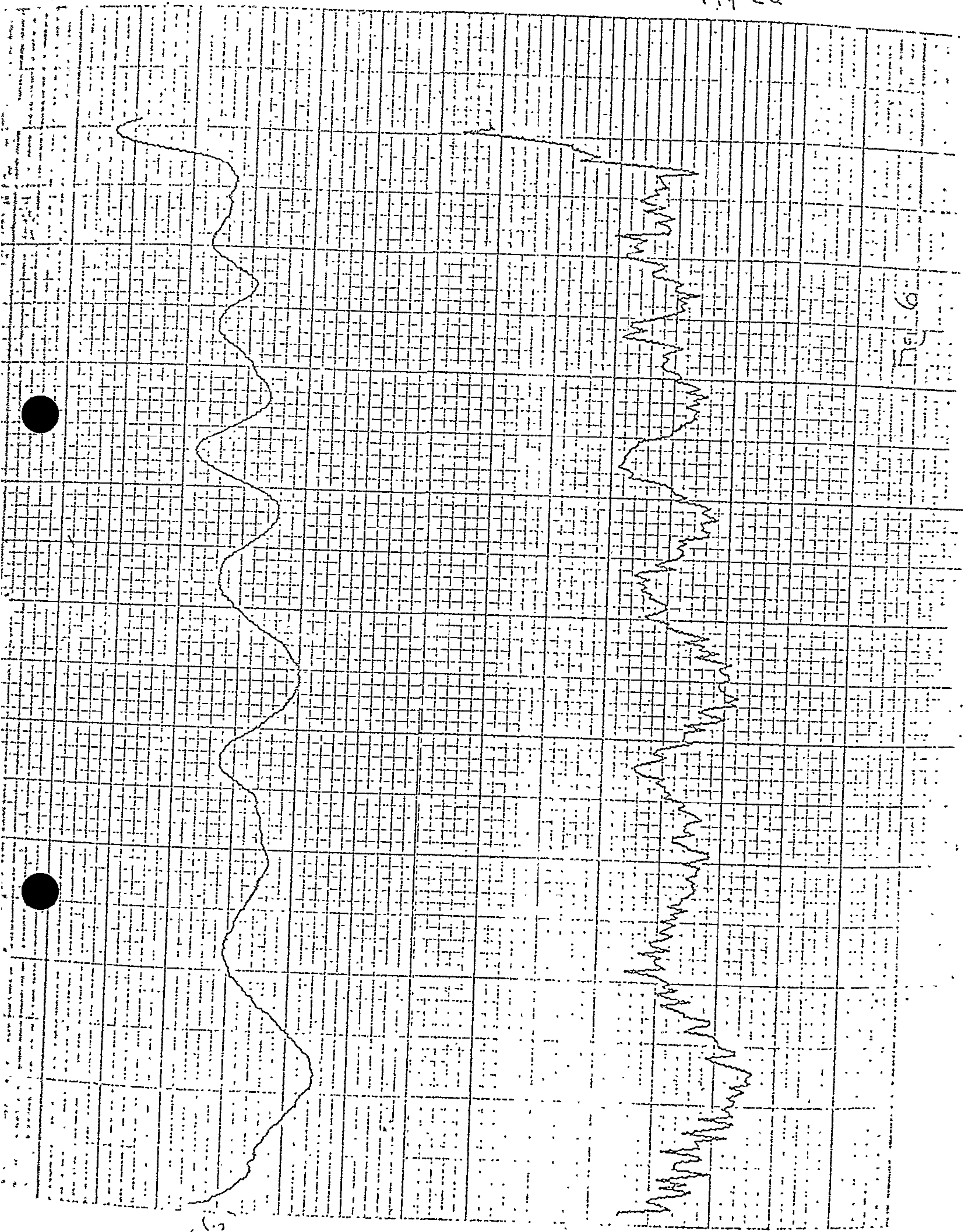


Fig 6

Figure C7 is another set of lunar runs. The lamp had been changed, and the magnet run down and the liquid helium replenished. Only two runs were obtained.

The corresponding background for set C7 is set C8. Figure C8 is the average of the first six of the set. Instrument settings were changed for the last two and the results are meaningless.

This set is reduced in Figures C9 and C10. These again are representations of the signal due to the lunar sample.

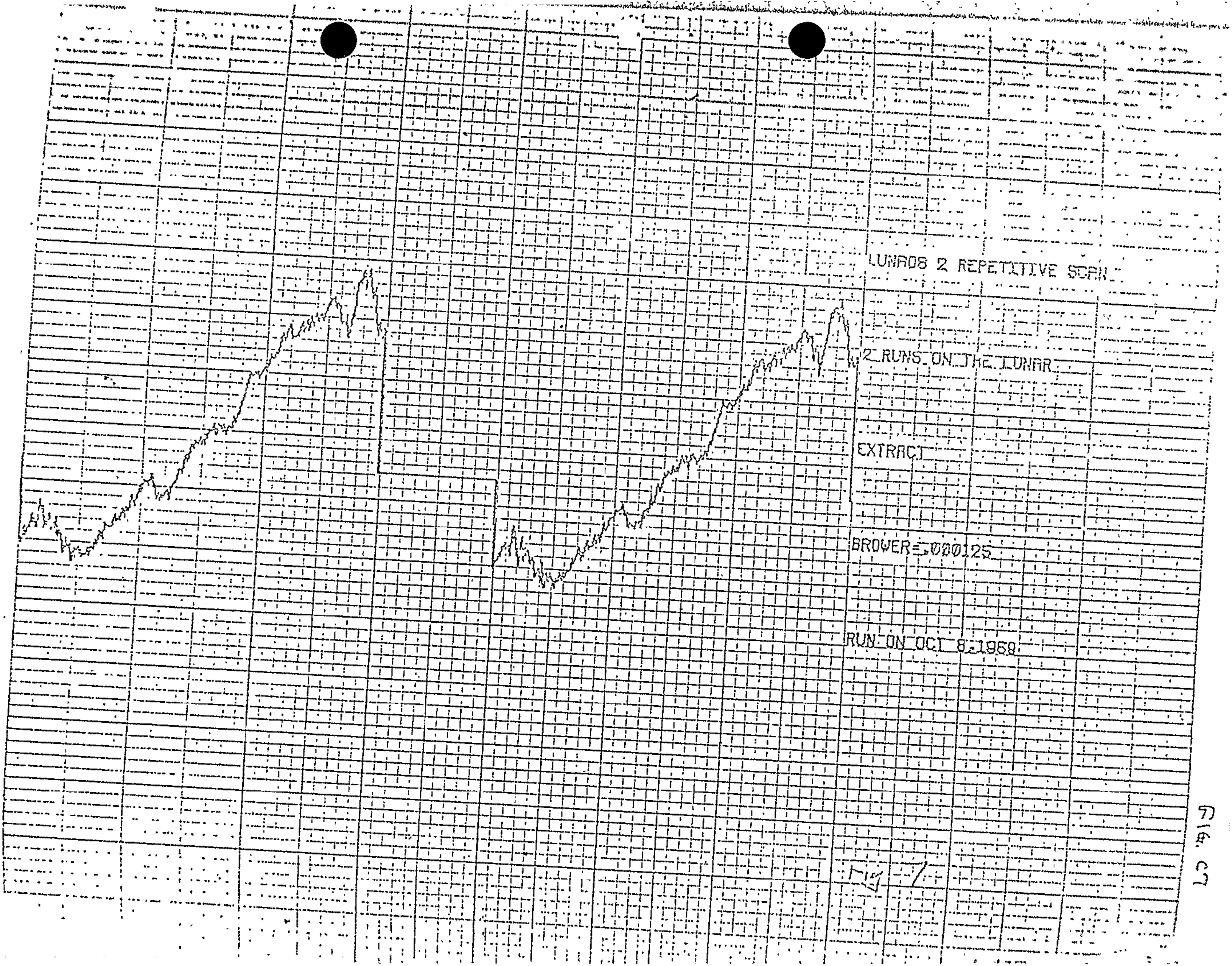

LUNA08 2 REPETITIVE SCAN
2 RUNS ON THE LUNAR
EXTRACT
BROWER=.000125
RUN ON OCT 8,1968

Fig 7

Fig. C7

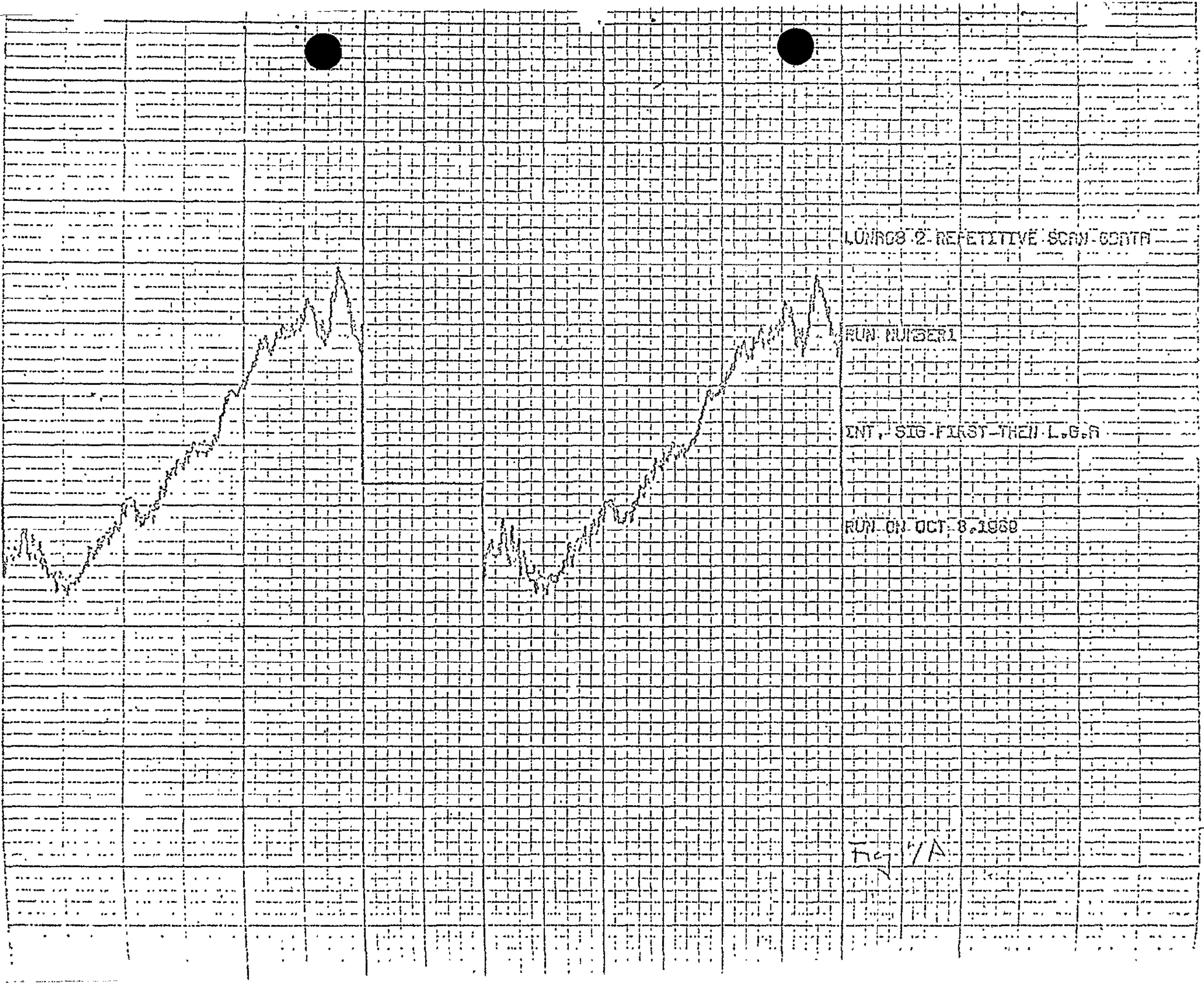


Fig 1/A

Fig CTC

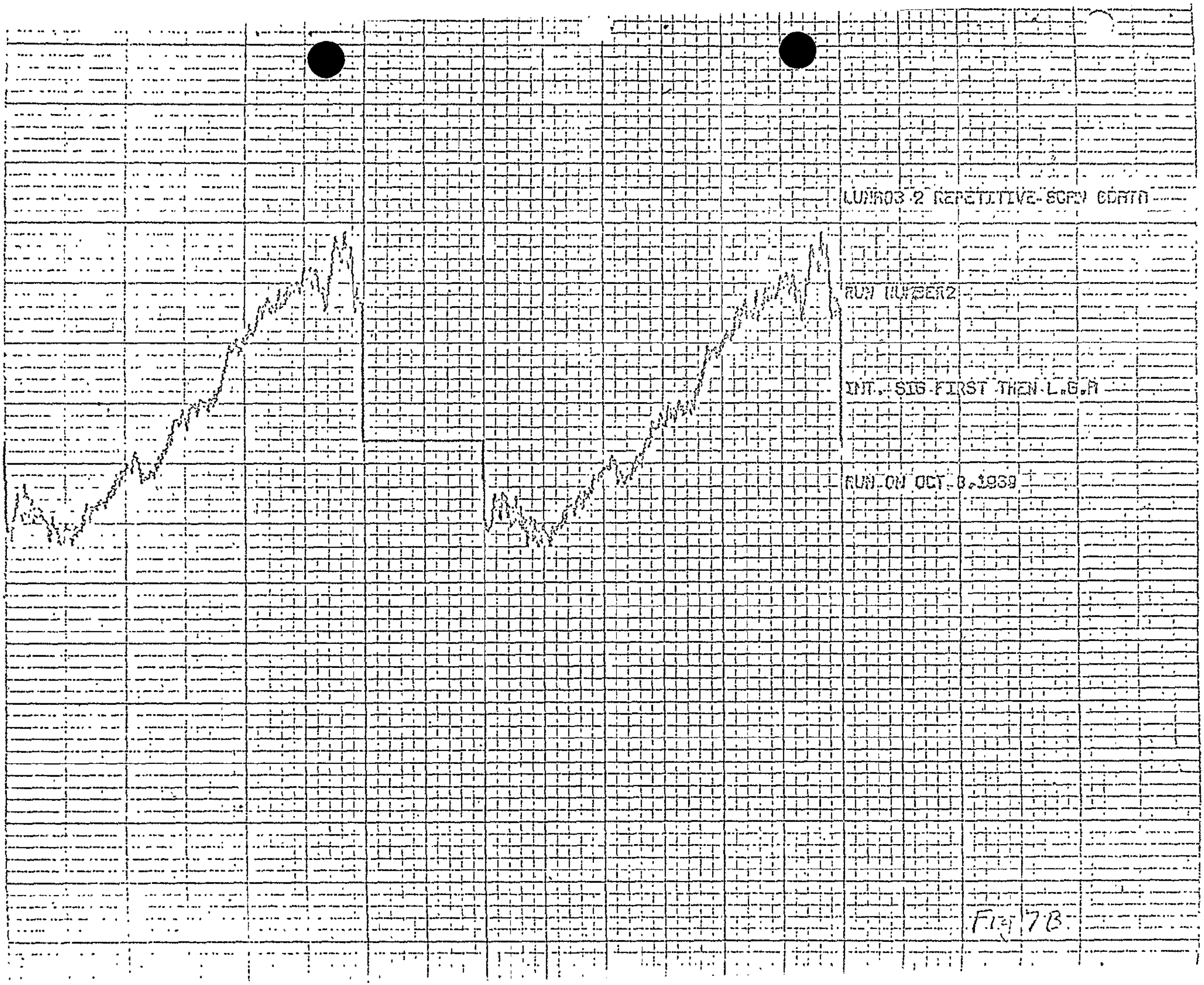
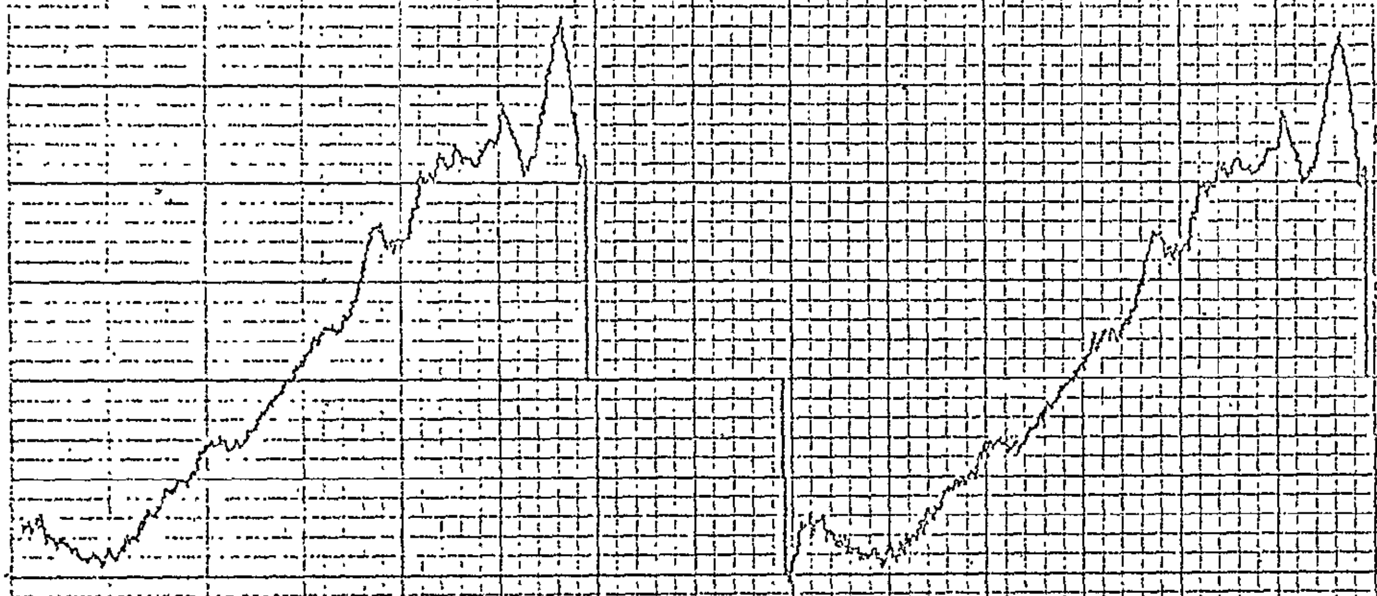


Fig 7B

Fig C7b.



MCD085K4. REPETITIVE SCAN OF EDATA

BASELINE AS LUNA03 4. FIRST IS AS.

SECOND IS LGA. FIRST 4 RUNS GOOD

BROWER=.000125, T=1 SEC

RUN ON OCT 8, 1969

Fig 8

Fig C8

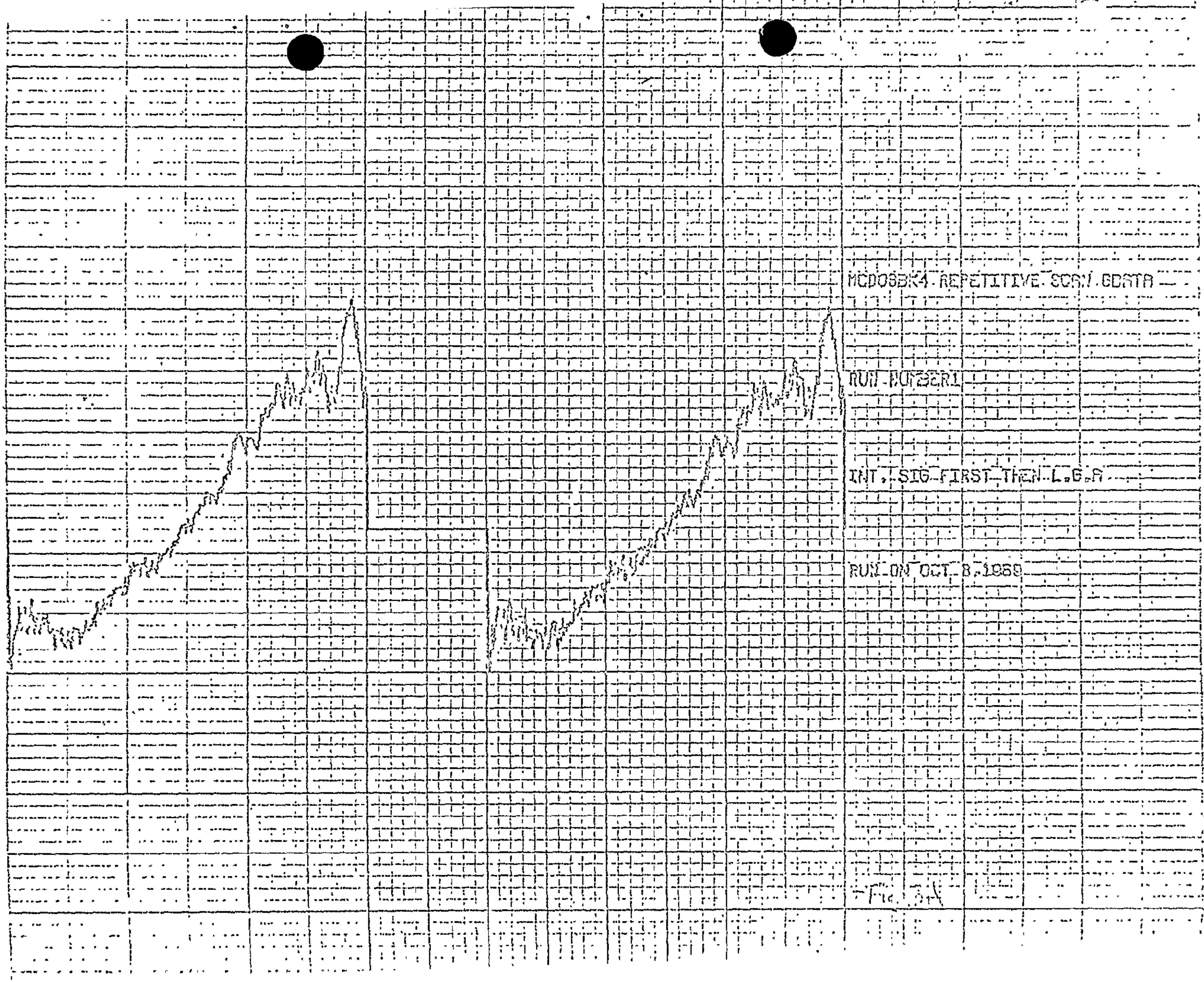

MCDOSBK4.REPETITIVE.SCAN.GDATA
RUN NUMBER1
INT. SIG FIRST THEN L.G.A
RUN ON OCT. 8, 1989

Fig. 3A

Fig (3

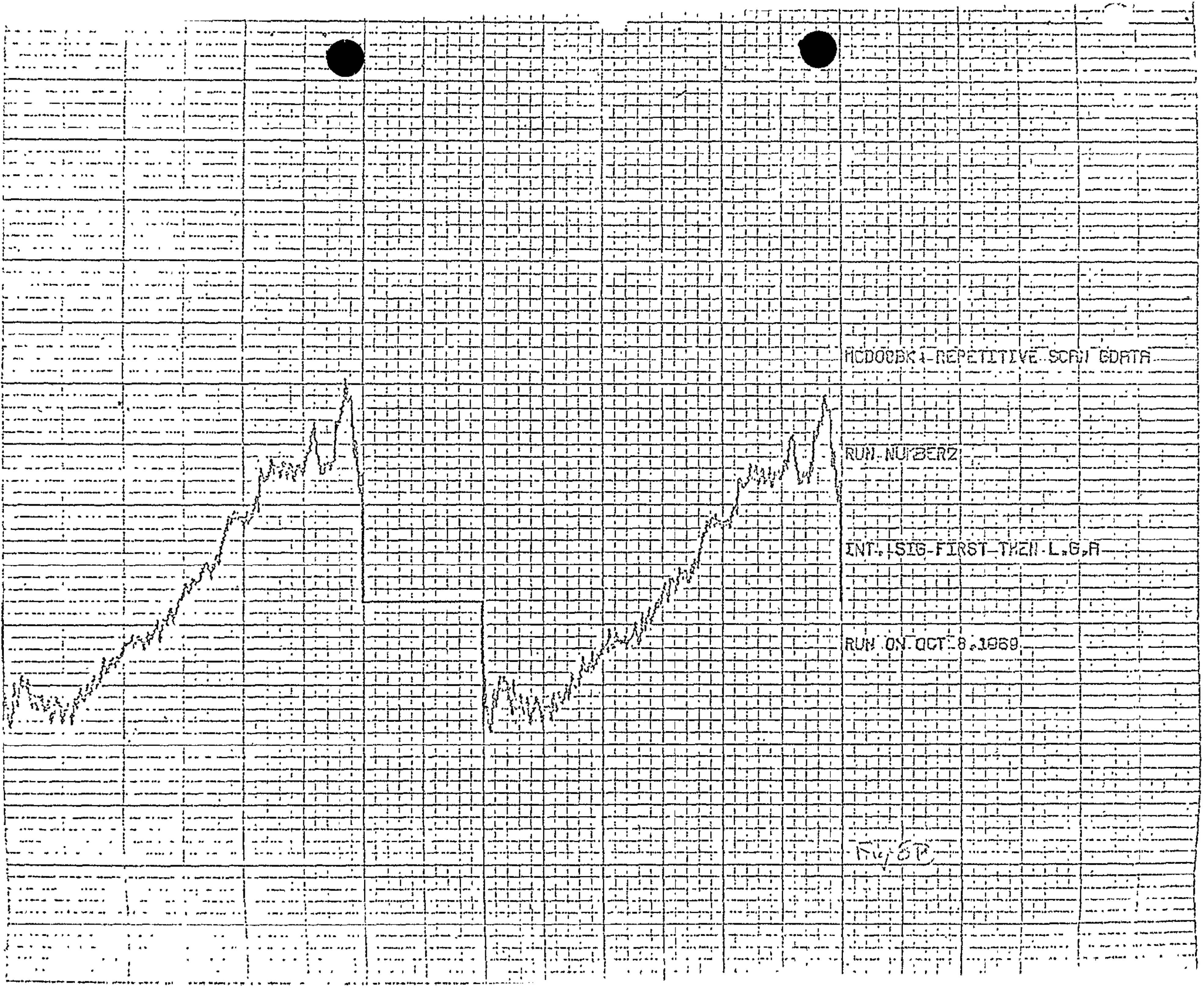


Fig 6B

Fig 6ab

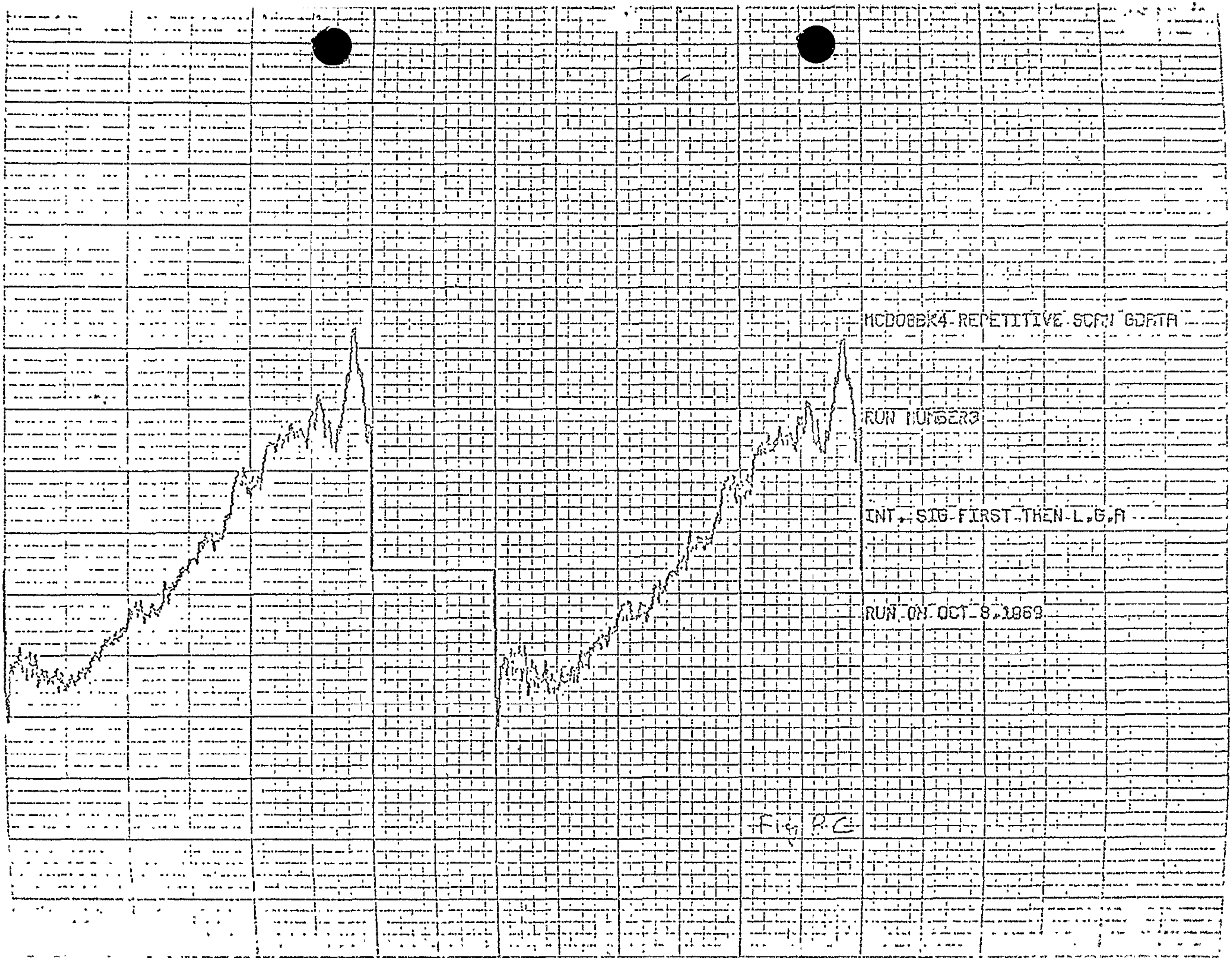


Fig 8C

Fig C 8c

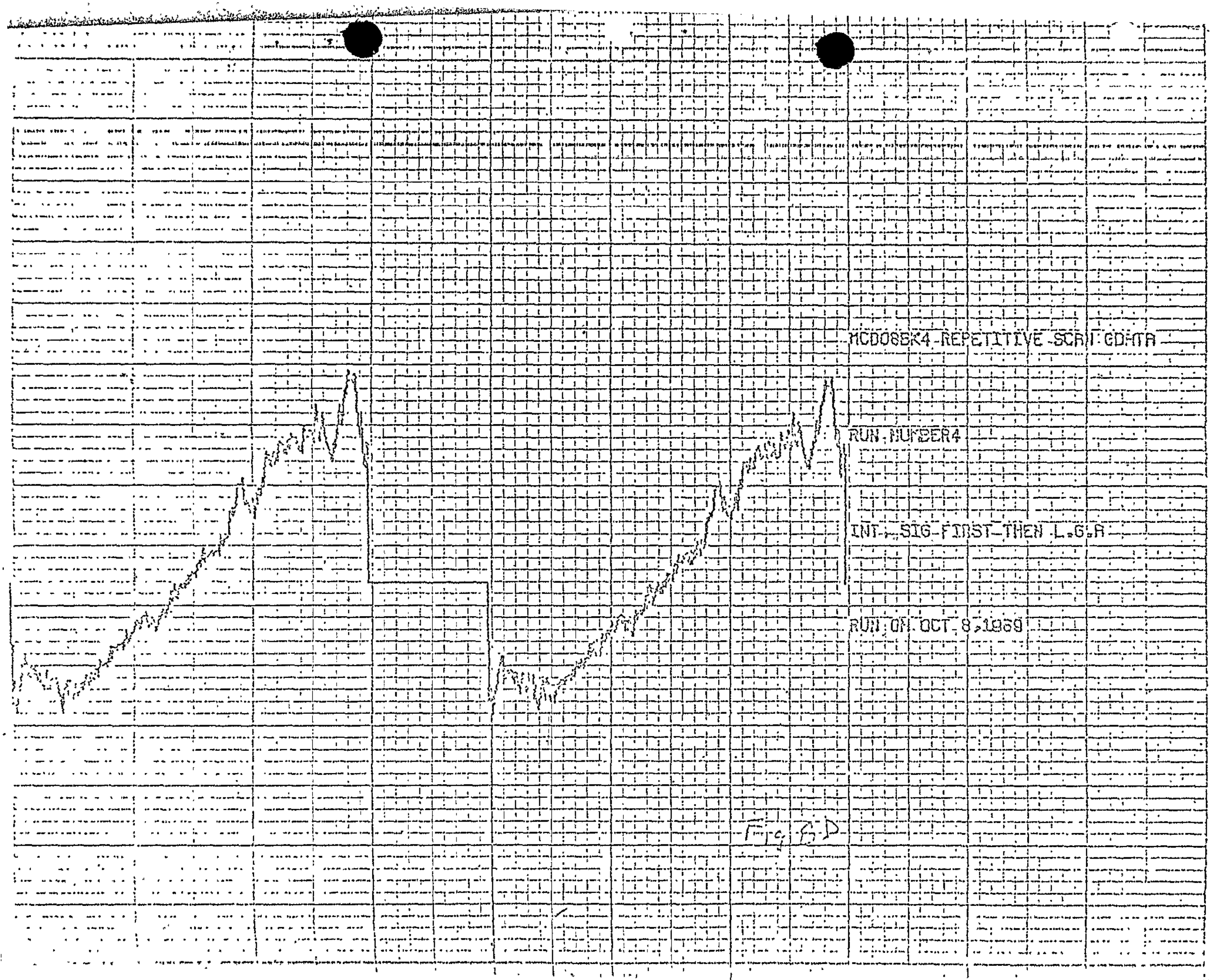
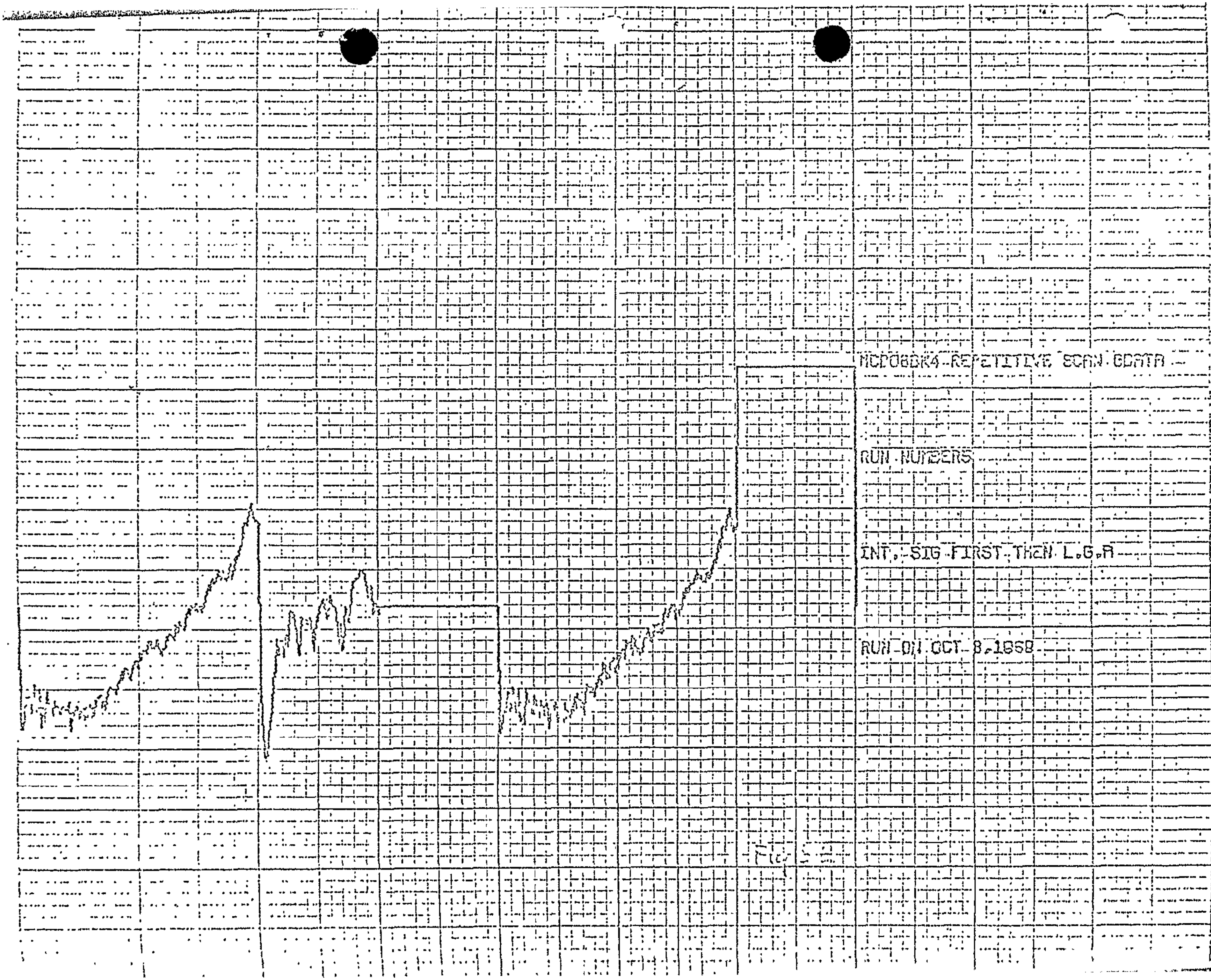

MCD08SK4 REPETITIVE SCAN DATA
RUN NUMBER4
INT. SIG FIRST THEN L.G.A
RUN ON OCT 8,1969

Fig 8D

Fig C8



MCP08BK4 REPETITIVE SCAN GDATA

RUN NUMBERS

INT, SIG FIRST THEN L.G.A

RUN ON OCT 8, 1968

Fig C8e

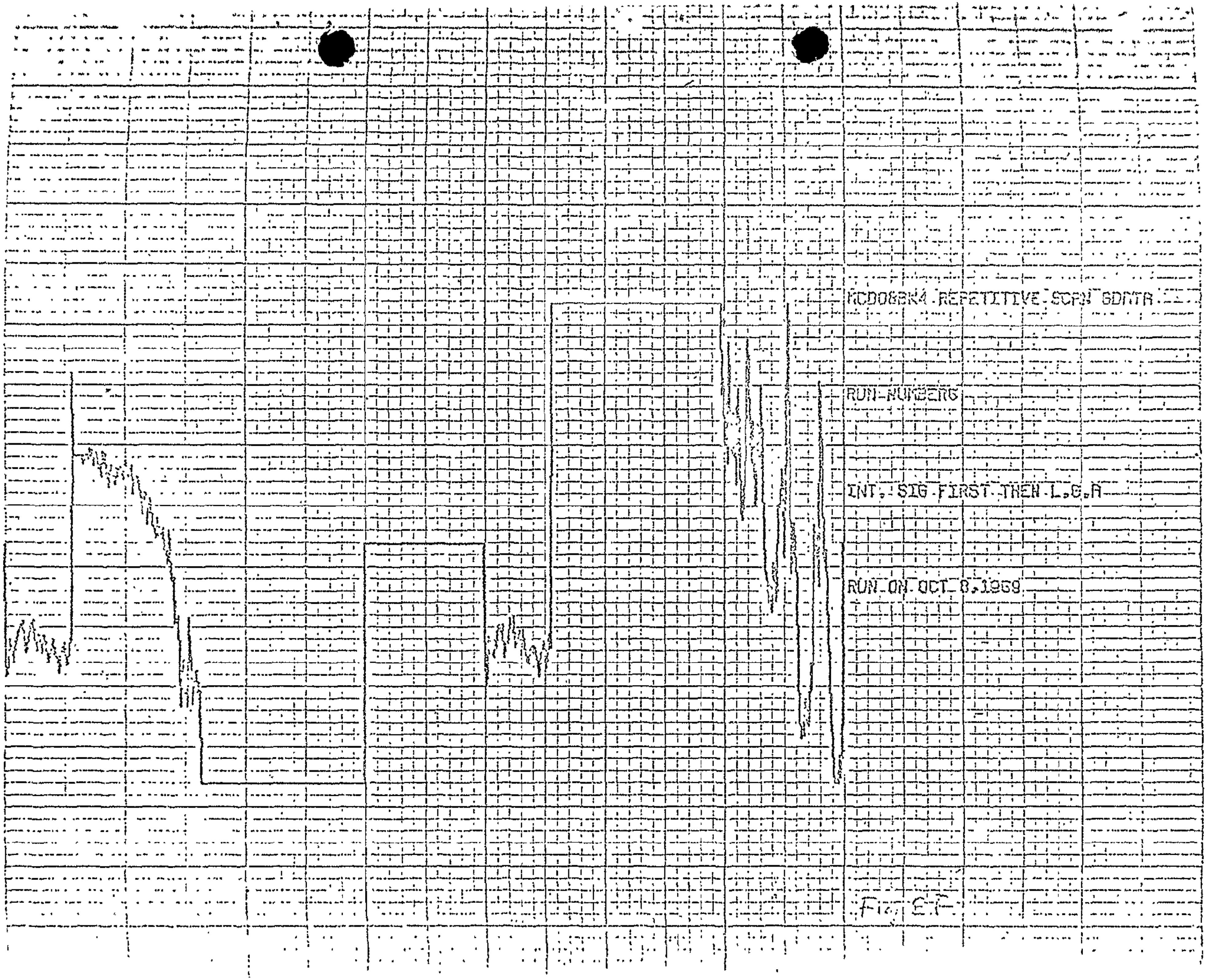


Fig. E.F

Fig C8 f.

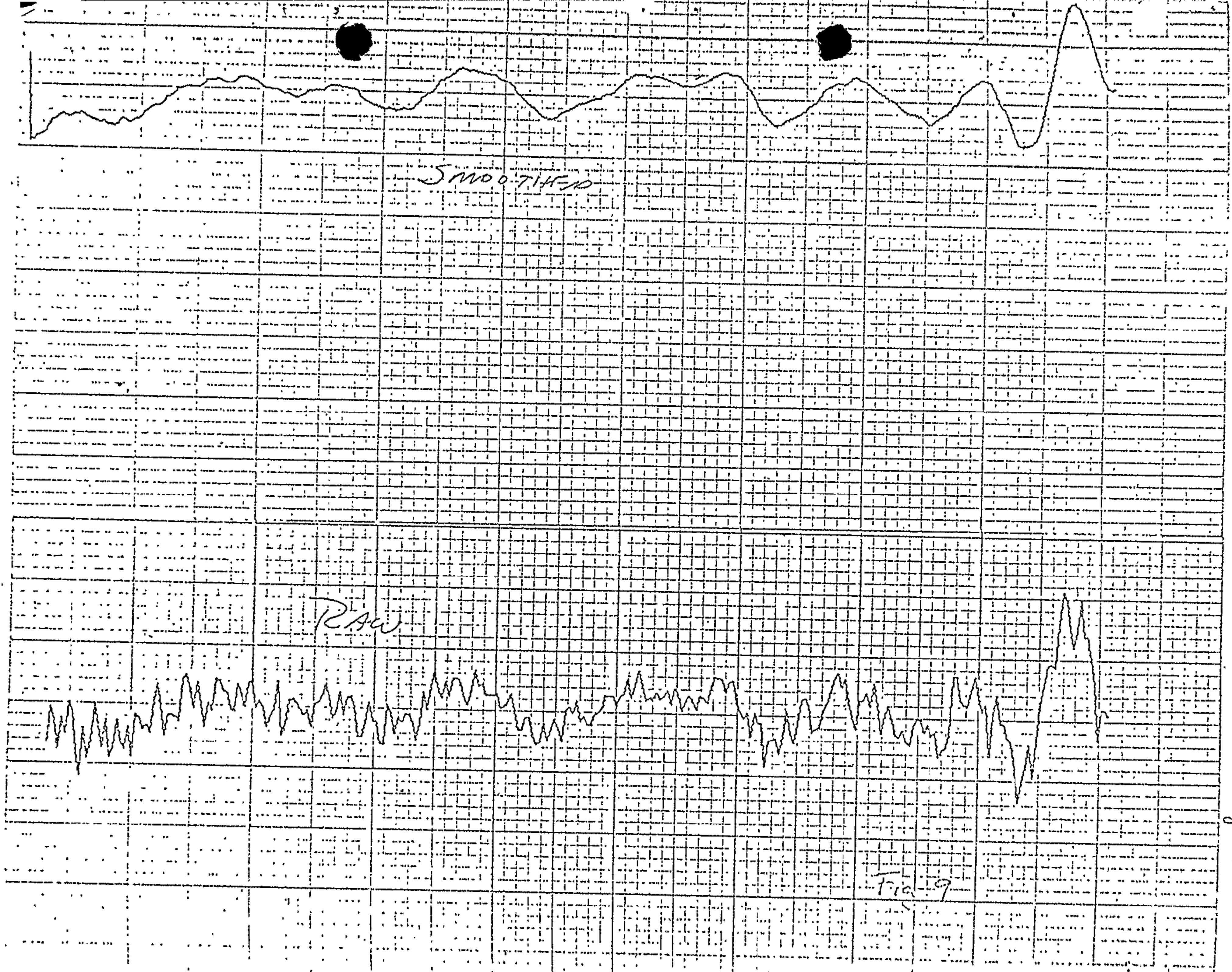


Fig 9

Fig 9

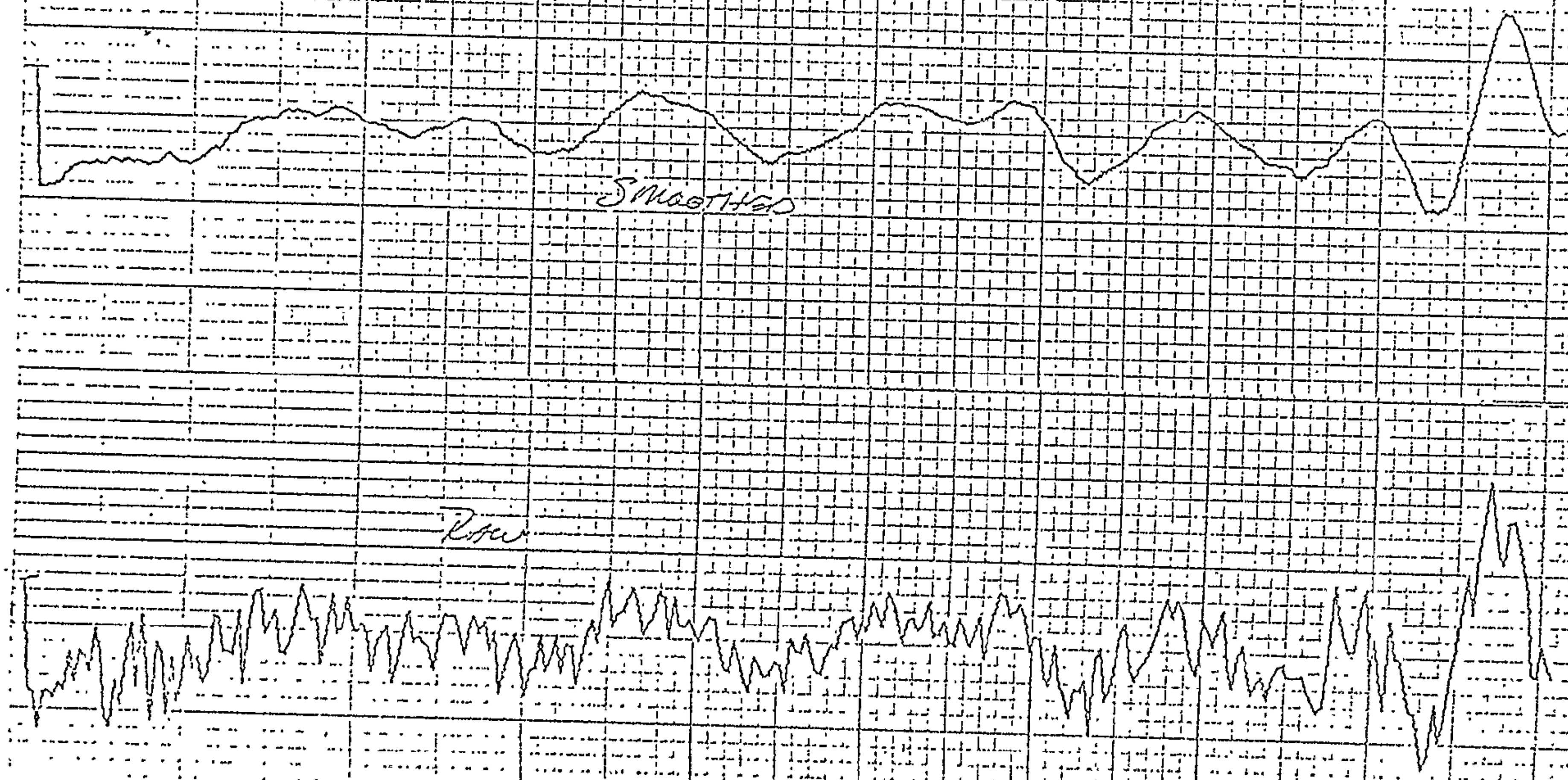


Fig 10

Fig 10

'04