DEPARTMENT OF
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BUREAU OF MINERAL RESOURCES, GEOLOGY AND GEOPHYSICS

Record 1970/11

STUDIES IN THE COLD EXTRACTION OF COPPER, LEAD, AND ZINC FROM GEOLOGICAL MATERIALS

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J.R. Beevers

(Revised and compiled by S.E. Smith)

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CONTENTS

SUMMARY

The results of this investigation indicate that cold extractable metal (cxMe) determinations on stream sediment samples provide no more, and possibly even less, information in a geochemical prospecting program than 'total' metal determinations. Particle size of the stream sediments affects both the 'total' metal and cxMe values, but not sufficiently to warrant recommending a change in sampling procedure from a -80 B.S.S. mesh.

Complex formation is fundamental to the determination of cxMe values. If complex-forming anions are absent, only the hydrogen ion is capable of causing the extraction of any appreciable amount of metal from the sediment. Commonly recommended weak or cold extractants, such as 0.1 M ammonium citrate, are almost as efficient as their concentrated solutions in the determination of cxMe values.

Drying out of a stream sediment before or after sampling only slightly affects the cxMe values obtained, provided equilibrium conditions are allowed to develop. Drying out of the sample however, does effect the rate at which equilibrium is reached, and in some cases it was found that equilibrium had not been reached after twenty days.

Metals being sought in stream sediments are commonly present in primary and secondary minerals. Not only are these measured in the 'total' metal content of the sediment, but also in the cxMe values. An attempt has been made to assess the relative rates at which recommended extractants react with some of the common minerals. It was found that primary sulphides are only slowly attacked, whereas secondary minerals, for example, azurite and malachite, are readily attacked.

Using 253 stream sediment samples from the Herberton area, north Queensland, it has been shown that the cxMe value is not simply related to the 'total' metal content. This is probably because of the different rates of attack by the weak or cold extractants used on them. Because of this lack of a simple relation, care should be taken before disregarding the results obtained from stream sediment sampling based solely on cxMe values.

The evidence suggests that meaningful comparisons of results from areas of different rock type may be made for both 'total' metal and cxMe values. It is the form the metal takes in the sediment (i.e., the mineralogy) that affects the cxMe values rather than the nature of the associated gangue material.

The procedure recommended for the sampling and analysis of stream sediments for geochemical prospecting is to use the -80 B.S.S. sample fractions, which may be dried in the field, and to analyse them by the aqua regia 'total' method.

INTRODUCTION

The increase in geochemical prospecting over the past fifteen years has been outstanding, and has resulted in a great increase in the number of chemical analyses required. Chemical analyses, in fact, consume a large part of the budget of any geochemical exploration program and, partly because of this, various studies have been carried out in attempts to attain the best information with the minimum expenditure. This particular investigation was carried out to find which method of analysing stream sediment samples gave the most useful information in geochemical prospecting.

Geochemical exploration for base metals such as copper, lead, and zinc, involves the chemical analysis of soils, stream sediments, waters, and residual rocks from areas that are considered favourable for mineralization. Apparently the Russians were the first to introduce the systematic collection and chemical analysis of samples of soil and weathered rock as a prospecting method in the early 1930's (Hawkes & Webb, 1962).

These workers used emission spectrographic methods for determining the 'total' metal content of the samples, and no attempt was made to be more specific as to where, or in what form, the particular metal was located in the sample. Although the geologist has only comparatively recently become interested in this particular problem, the soil scientist has been interested in it for decades. For instance, it has been known for over a century that the content of a particular element in a soil includes that which is available by simple extractions and that which is tightly held in certain mineral lattices. Thus there is a difference in the amount of available element and the total content of the element in the soil. It was not until 1914 that the first recorded attempt was made to distinguish and to actually measure the difference (Gedroits, 1914). Gedroits proposed the use of dilute hydrochloric acid to determine 'exchangeable'* cations. This proposal was followed by Hissink (1923) who used 1 M ammonium chloride as an exchanger, and Williams (1928) who proposed the use of a weakly dissociated acid, 0.5 M acetic acid, for the same purpose. These wers were only determining what they called 'exchangeable' Ca, Mg, Na, K, and H, and to a lesser extent Fe, Al, and Mn.

Subsequent methods used to measure available or extractable ions can be traced mainly to these early workers.

The earliest report of a weak extractant being used in geochemical prospecting is that of Lovering et al. (1948) who used a cold acetate extracant in order to 'remove only those heavy metals presumably related

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* What was actually measured was extractable cations, as will be made clear later in this report.

to mineralization, not the total metal content of the rock'. Bloom (1955) proposed ammonium citrate because it extracted base metals from soils, and it provided a suitably buffered solution to carry out analysis for Cu, Pb, and Zn by colorimetric techniques.

The present study was carried out in an attempt to obtain a clearer understanding of the meaning of 'cold extractable metal' than previously available, and to assess its value in geochemical prospecting.

INVESTIGATIONS INTO COLD EXTRACTION METHODS FOR GEOCHEMICAL PROSPECTING

The study was divided into five phases.

(1) Selection of the most suitable extractant, extraction time, and sample particle size.

(2) Effect of extractant concentration on cxMe values.

(3) Effect of drying out the sample on cxMe values.

(4) Influence of primary and secondary minerals on cxMe values.

(5) Relationships between cxMe and 'total' metal content.

Analyses were carried out by atomic absorption spectrophotometry using calibrating solutions in a medium appropriate to the extractant being used.

(1) Selection of extractant, extraction time, and sample particle size

Many people involved in geochemical prospecting make the basic assumption that the best extractant is the one that gives a cxMe value closest to the total content for any particular metal. The following discussion will show that this is not necessarily so.

For the particular study dealt with in this section, two bulk samples (A and B) of wet stream sediment material were collected in quite different geological settings, although each was known to contain a substantial amount of extractable metal.

Sample A was obtained from Sapphire Creek, 29 km east of Port Moresby, P.N.G. The drainage pattern of this stream covers calci-lutites, gabbros, and agglomerates. There are two old copper mines in the area, upstream from this sample location.

Sample B was collected from a stream draining into Paddy's River, approximately 23 km west of Canberra. This stream drains a porphyry and skarn zone. Two collapsed adits with accompanying dumps from small copper, lead, and zinc outcrops occur about 400 m upslope from the sample point. A detailed mineralogical examination of the two samples was made by I.R. Pontifex, and this is given in Appendix A.

About 5 Kg of -80 B.S.S. fraction of each stream sediment was wet-sieved in the field and stored under water. In the laboratory, the samples were further wet-sieved through 120 B.S.S. and 200 B.S.S., retaining each fraction. The -200 B.S.S. fraction was further separated into +20μ and -20μ fractions by sedimentation. The four size fractions of samples A and B were kept under water when not in use. A dried part of each size fraction was anlysed for 'total' copper, lead, and zinc using an aqua regia digest, and the results, expressed as parts per million of the dry weight, are shown in Table 1. 'Total' lead was found to be less than 20 ppm in all the fractions of both samples, and no further interest was taken in this.

Several aqueous extractants were studied, some containing strong complex forming anions, and others containing only weak or non-complexing anions. Table 2 shows those studied, the concentrations used, and the pH of each solution before the extractions were made.

Approximately 2 g of the wet 80-120 B.S.S. fraction of sample A and 40 ml of 0.5 M ammonium citrate were put into a 50 ml screw cap test tube. This was repeated using each size fraction of each sample with each extractant, making a total of 72 tubes which were arranged in panels attached to an end-over-end shaking machine, and rotated at 6 revolutions per minute.

After they had been shaken for one hour the samples were left to stand for about 30 minutes to allow the supernatent liquid to clarify. Sample A was analysed for copper and zinc, sample B for zinc only. The samples were then reshaken and analyzed after 24 hours. Shaking was then continuous except when analyses were being made at 2, 4, 7, 11, and 17 days after the start of the experiment.

At the conclusion of the experiment the contents of each of the tubes were filtered, washed, air dried, and weighed. The results were computed in terms of dry weight of sample and plotted in Figures 1-8. Extraction values at equilibrium were read from these figures and are shown in Tables 3-5. It can be seen that for samples A andB, 0.1 M hydrochloric acid is the most efficient extractant tried with 0.25 M EDTA next followed by 0.5 M ammonium citrate and 0.5 M sodium tartrate.

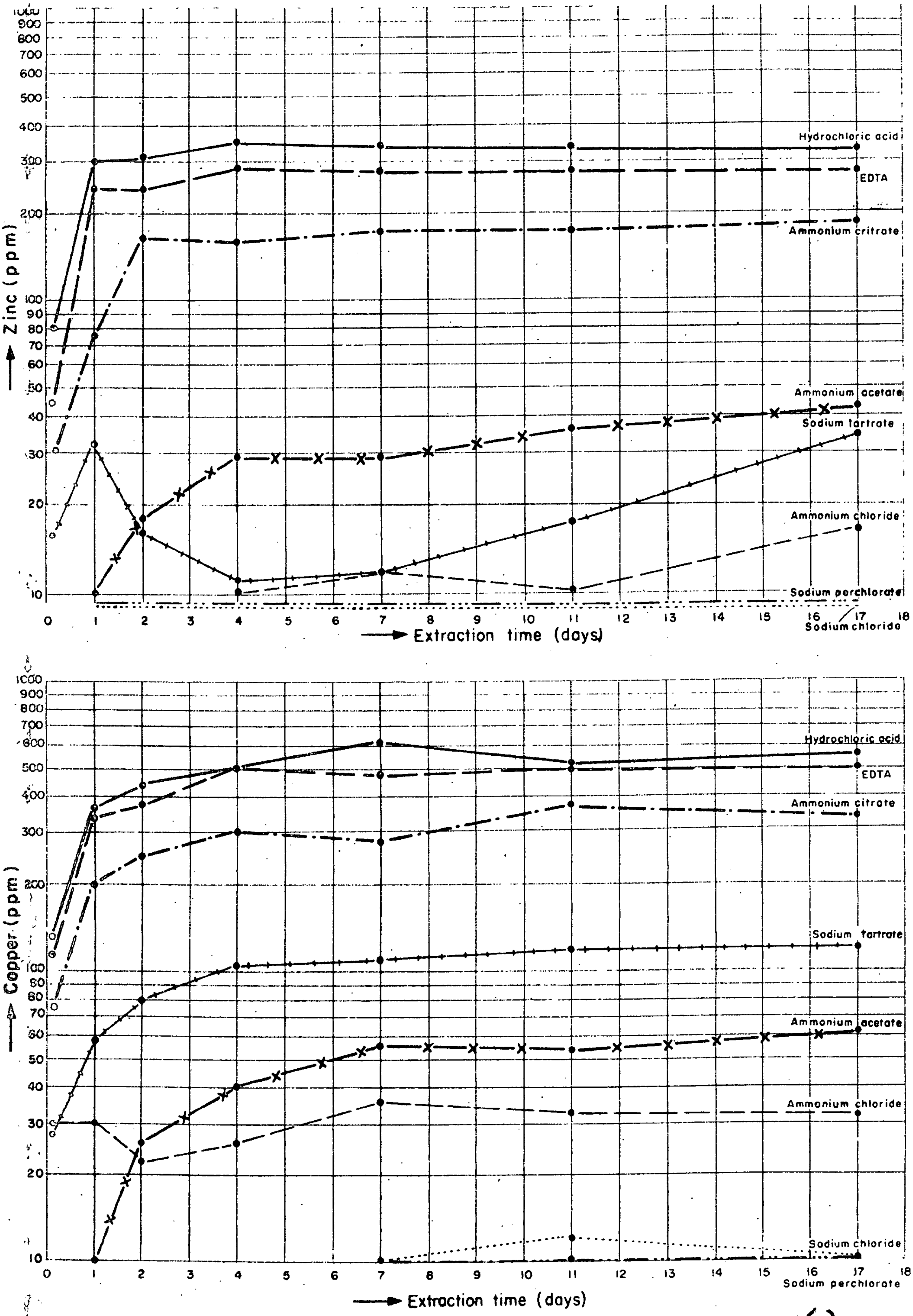

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Fig 1 Extraction of copper and zinc from the 80-120 B.S.S. fraction of sample A by various extractants.

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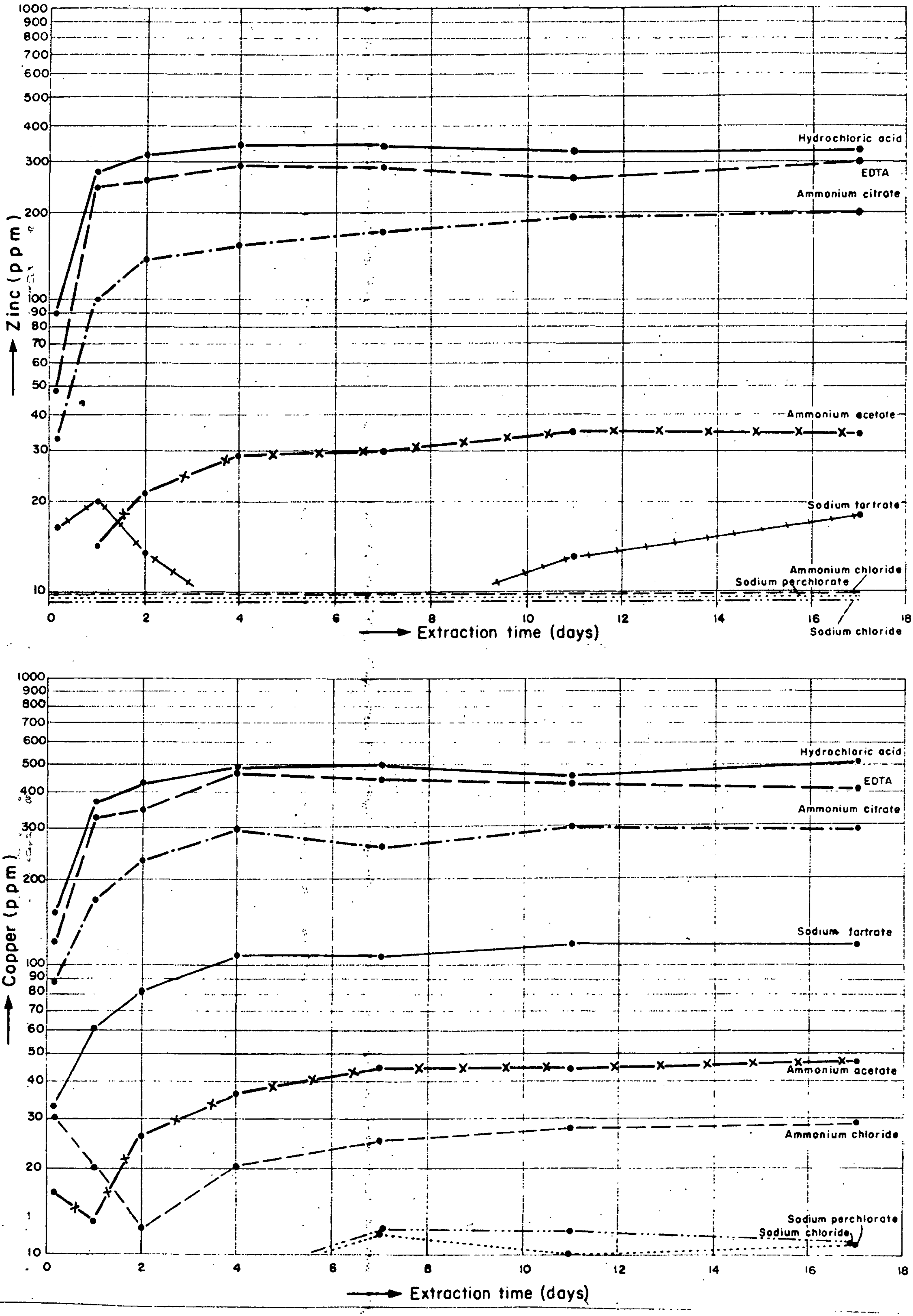

Fig 2. Extraction of copper and zinc from the 120-200 B.S.S. fraction of sample A by various extractants.

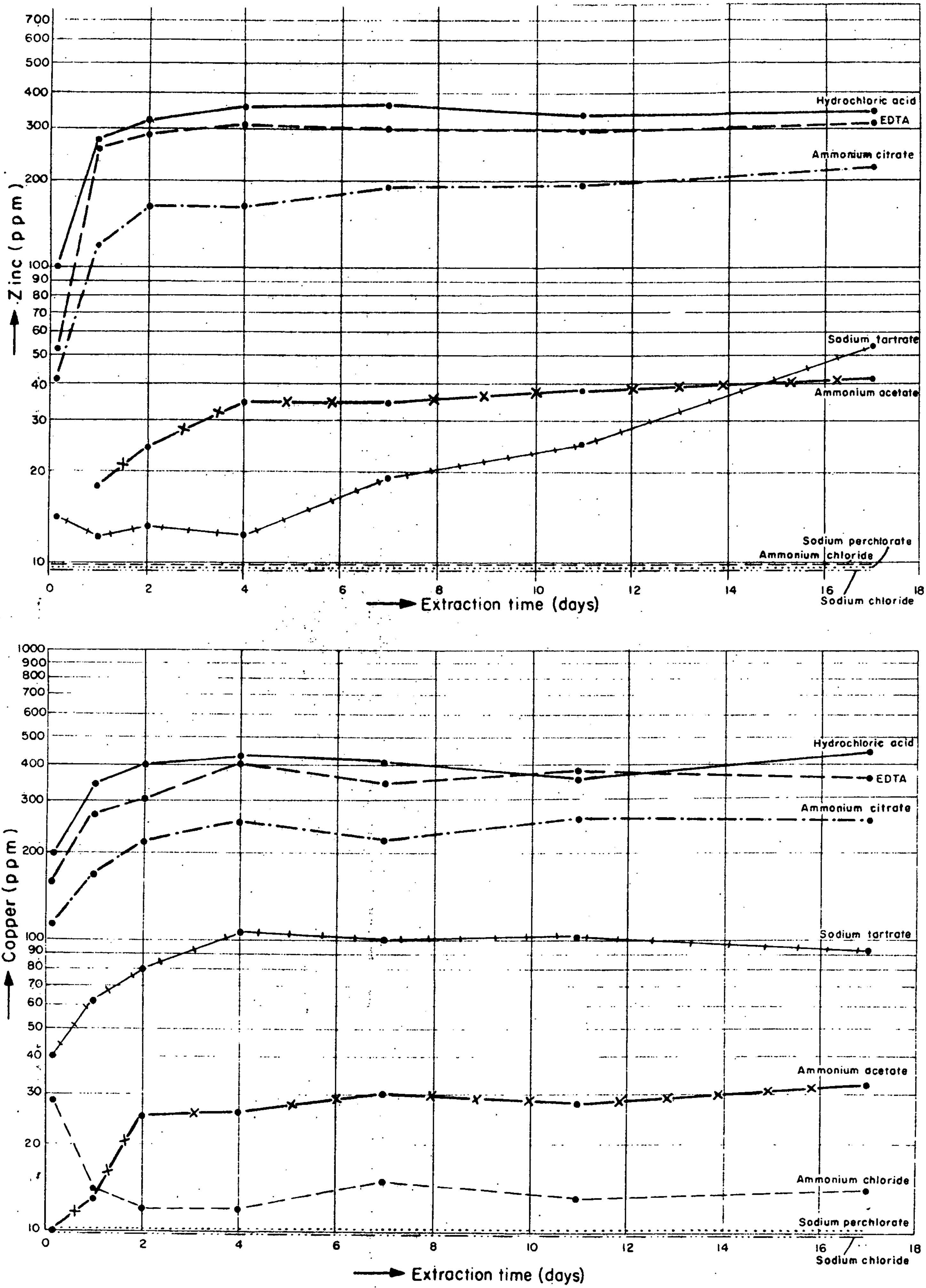

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Fig. 3. Extraction of copper and zinc from the 200 B.S.S. - 20μ fraction of sample A by various extractants

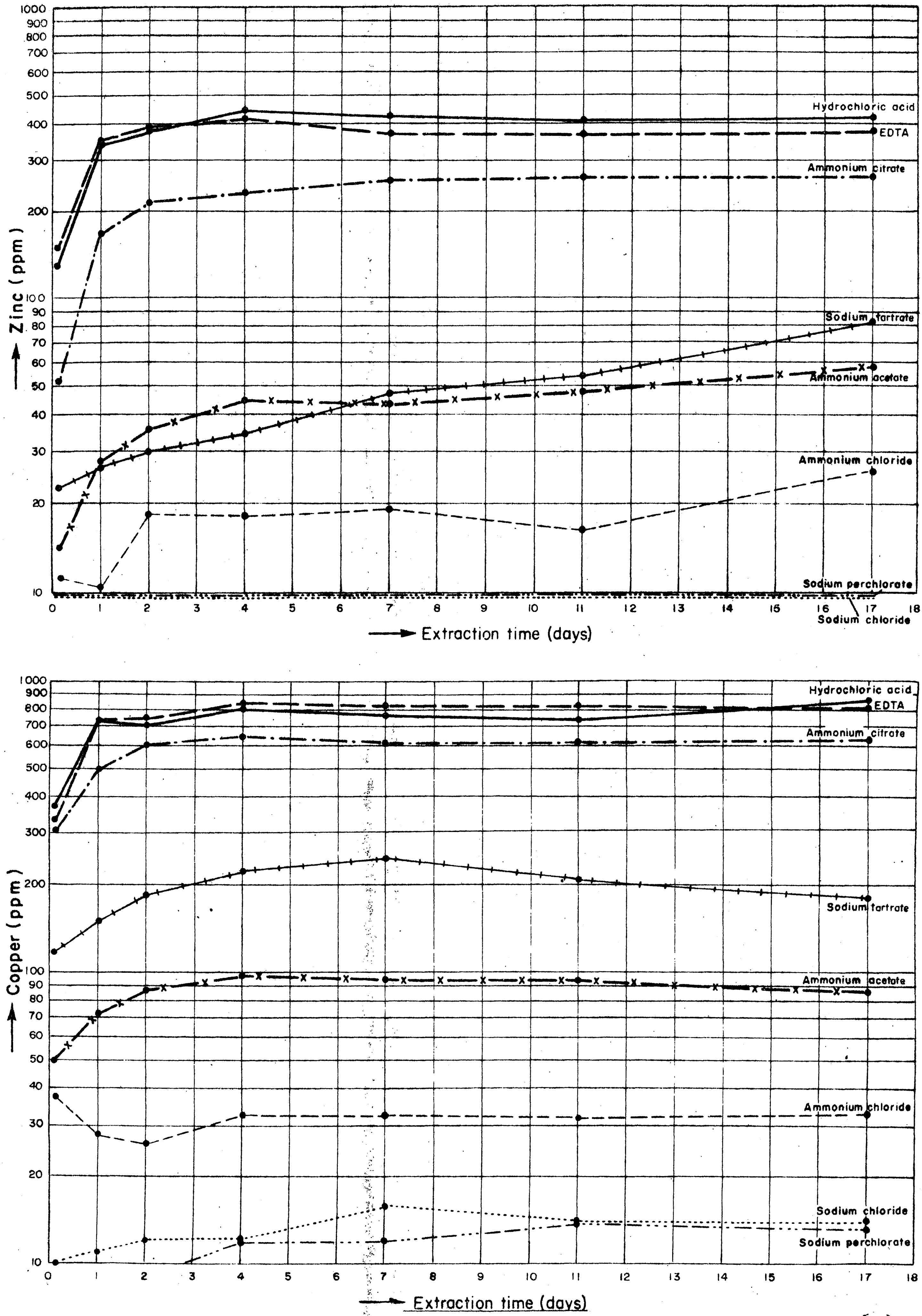

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Fig 4. Extraction of copper and zinc from the - 20μ fraction of sample A by various extractants

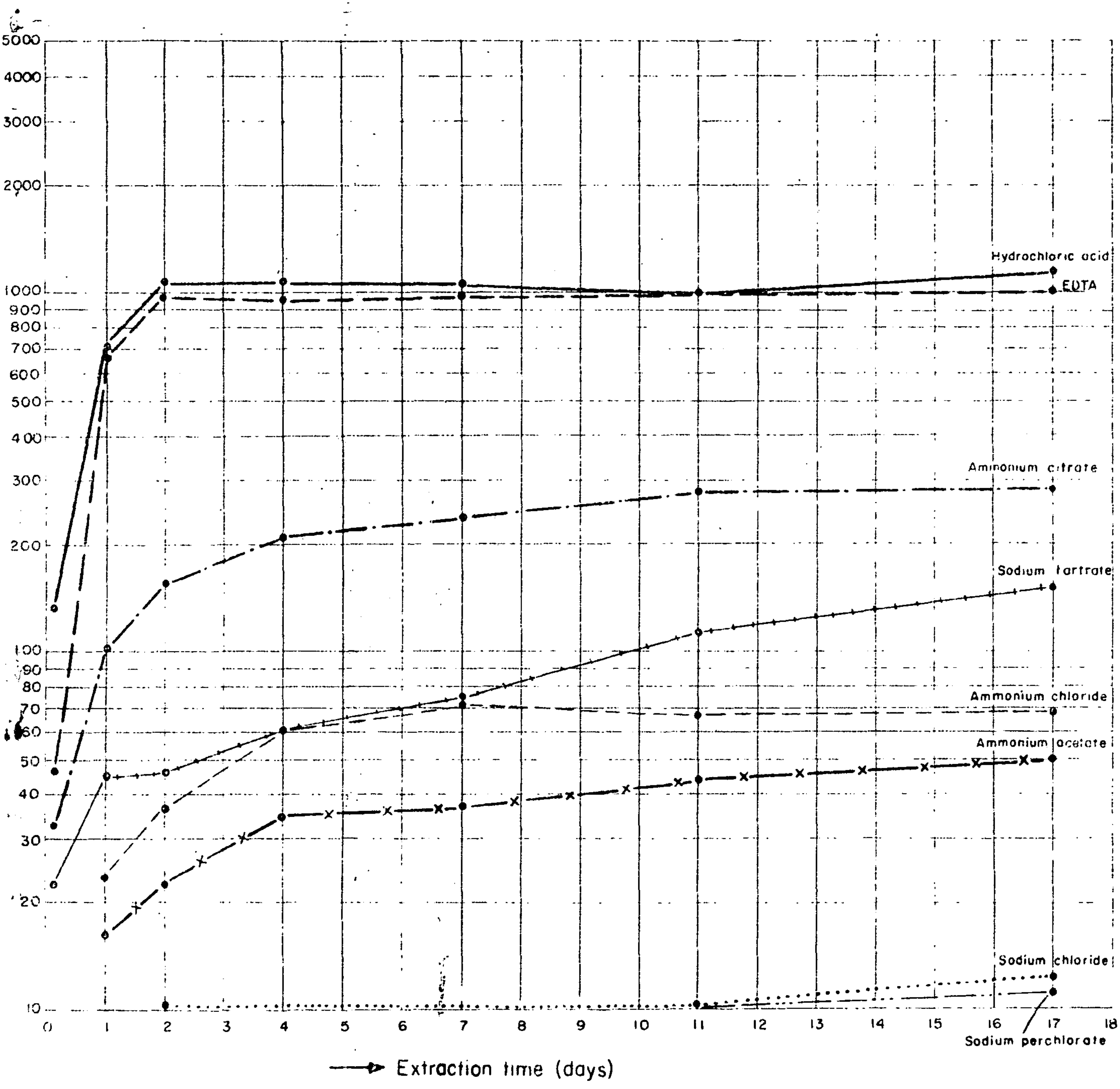

Fig. 5. Extraction of zinc from the 80-120 B.S.S. fraction of sample B by various extractants.

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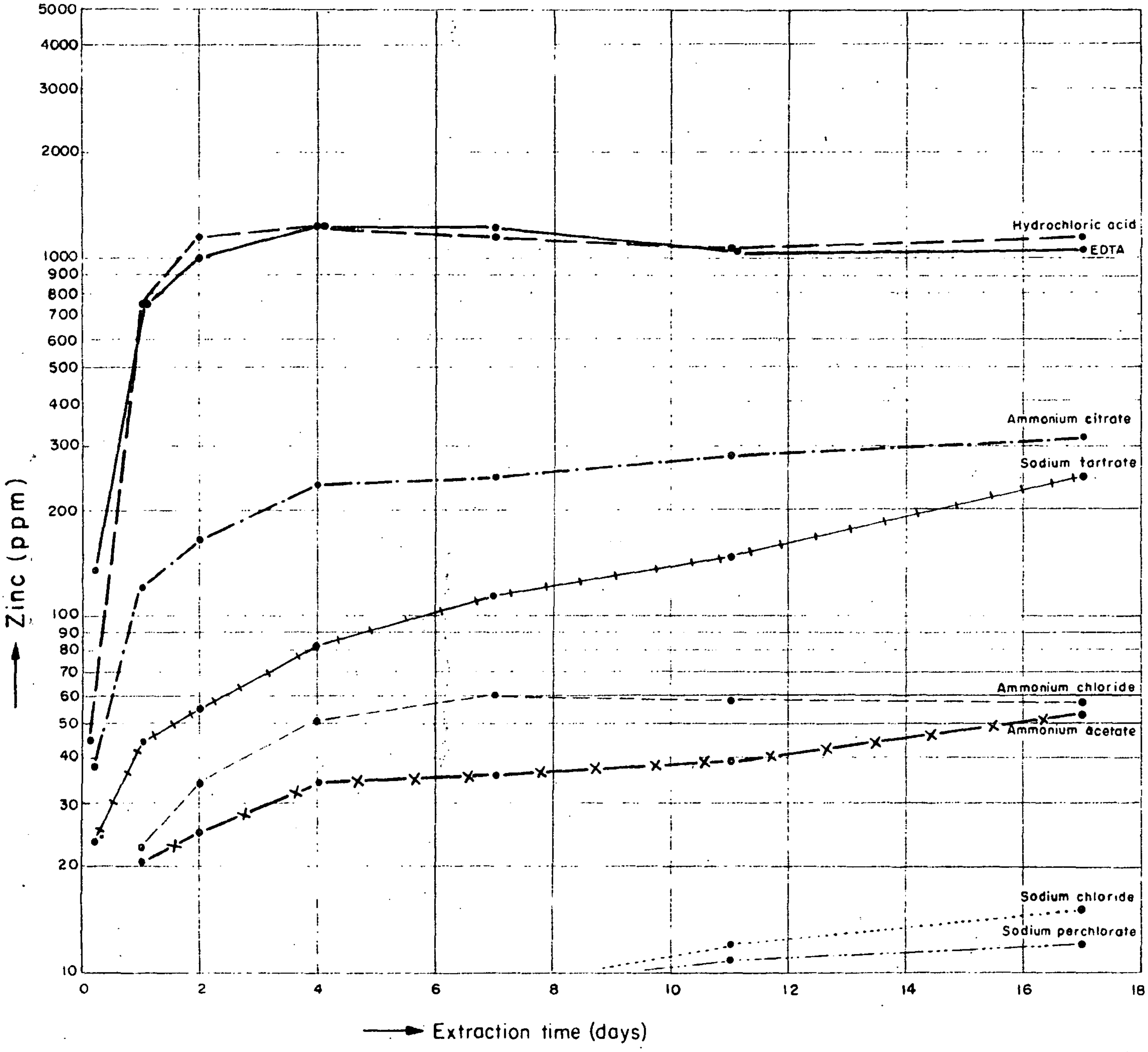

Fig 6. Extraction of zinc from the 120-200 B.S.S. fraction of sample B by various extractants.

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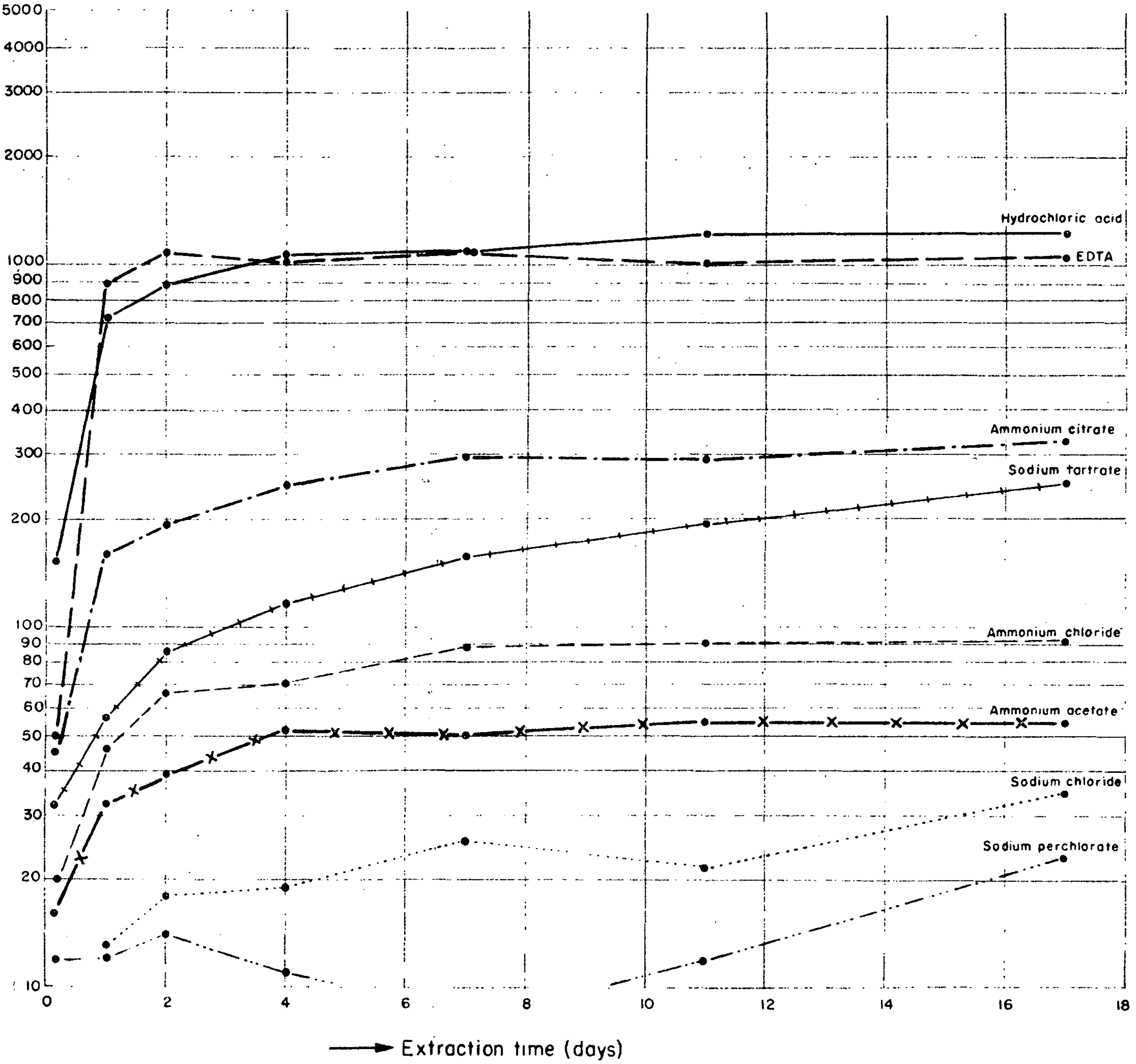

Fig 7. Extraction of zinc from the 200 B.S.S. - 20μ fraction of sample B by various extractants.

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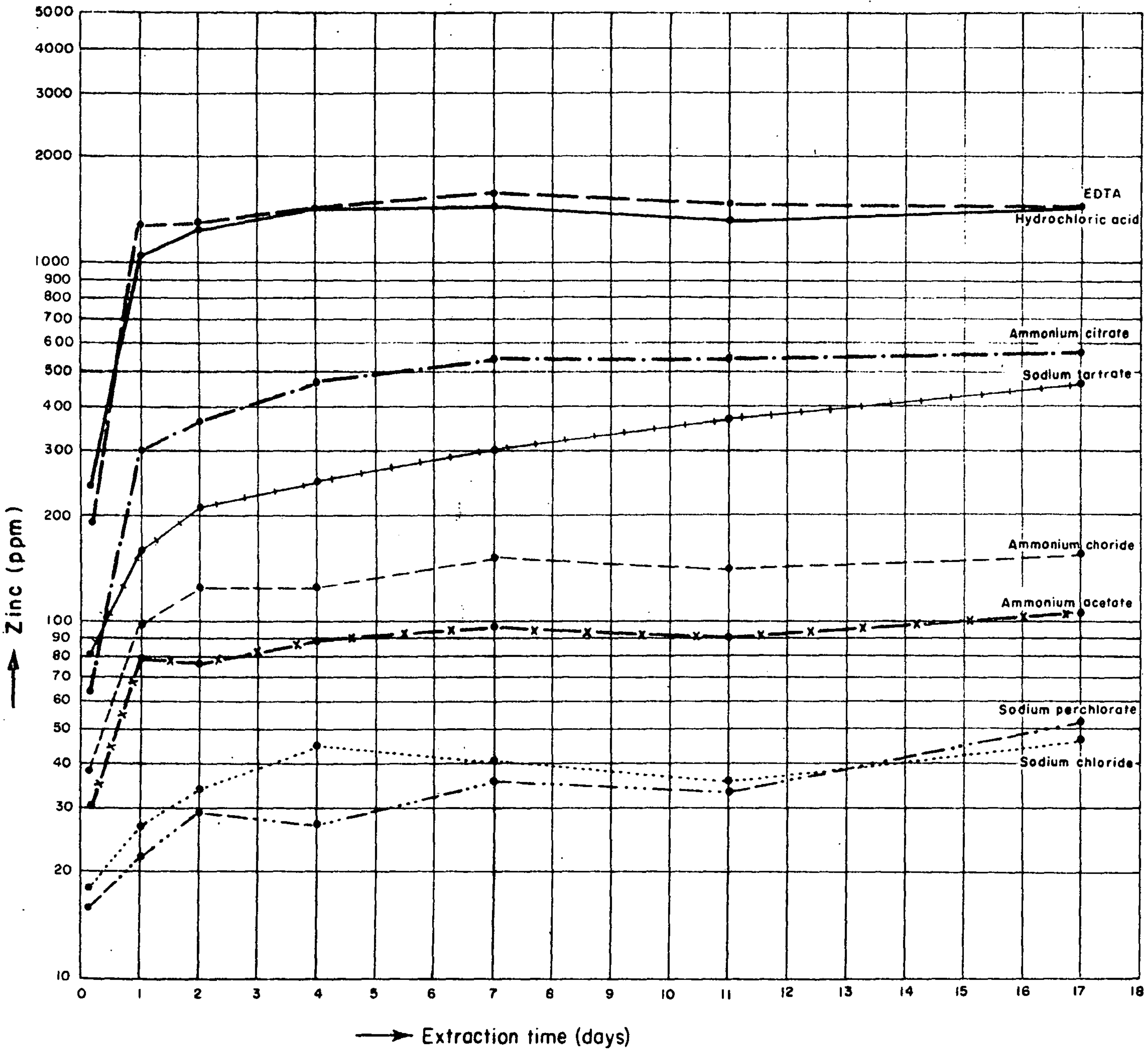

Fig 8. Extraction of zinc from the -20μ fraction of sample B by various extractants.

To accompany Record 1970/11

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TABLE 1. TOTAL METAL CONTENT OF SIZE FRACTIONS OF SAMPLES A AND B

Size Fraction		Total Copper (ppm)		Total Zinc (ppm)	
		Sample A	Sample B	Sample A	Sample B
80 B.S.S. - 120 B.S.S.	(190 μ - 125 μ)	1087	20	573	13
120 B.S.S. - 200 B.S.S.	(125 μ - 75 μ)	1030	30	555	1630
200 B.S.S. - 20 μ	(75 μ - 20 μ)	807	24	550	1350
- 20 μ		1052	35	625	1650

TABLE 2. EXTRACTANTS USED IN EXPERIMENTS TO FIND THE MOST SUITABLE EXTRACTANT

Extractant	Concentration (M)	pH
Ammonium citrate, $(NH_4)_3C_6H_5O_7$	0.5	6.92
Ammonium acetate, $NH_4C_2H_3O_2$	1.0	7.10
Sodium tartrate, $Na_2C_4H_4O_6$	0.5	7.48
Ammonium chloride, NH_4Cl	1.0	5.73
Sodium perchlorate, $NaClO_4$	1.0	5.42
Sodium chloride, NaCl	1.0	5.53
Di-sodium salt of EDTA	0.25	4.47
Hydrochloric acid, HCl	0.1	1.22
Distilled water, H_2O		5.70

Some additional points should be noted from the results. The magnitude of the truly exchangeable copper and zinc in the samples can probably be judged from the extraction values at equilibrium using M sodium perchlorate or M sodium chloride as extractants.

Only when the extractant contains a complex-forming ion (or the pH of the solution is low) is a significant amount of copper or zinc extracted from either sample. It appears that the stronger the complex formed between the metal and the ligand the better the extraction. From the present results one would expect the strength of both the copper and the zinc complexes to be in the order EDTA $>$ citrate $>$ tartrate and this is in fact the order of the stability constants.

The particle size of the stream sediment affects how much copper and zinc can be extracted. For the three coarser fractions the effects are small; however, the -20μ fraction generally shows a greater proportion of extractable zinc and, for sample A, a higher value for copper.

Complete extraction of copper and zinc from samples A and B took much longer than the extraction period of a few minutes commonly in use in geochemical prospecting. If samples A and B are taken as typical stream sediments, several days extraction is required to arrive at equilibrium conditions rather than a few minutes. The results recorded in Figures 1-8 indicate that a minimum of 2 days is required to achieve 80-90 percent of the true equilibrium extraction value even for the strongest extractants EDTA and hydrochloric acid. Equilibrium conditions were not achieved even after 17 days for the tartrate extraction of zinc, but no reasons for this unexpected behaviour can be advanced at present.

To confirm this result the experiment was repeated on a second sample B, sampled at a different time of the year, but using only 0.01 M EDTA/0.1 M sodium chloride and 0.5 M ammonium citrate as extractants. In this experiment, analyses of the supernatant liquid were made at more frequent intervals in the first day of extraction. The results are shown in Figure 9; the experiment was terminated on the second day of extraction. It can be seen that the EDTA extractant reached equilibrium (in this case complete extraction) in less than one day. The 0.5 M ammonium citrate extraction, however, was presumably incomplete after two days, in agreement with the previous results on sample B. It would seem that a minimum time of one day must be given for the extraction of stream sediments.

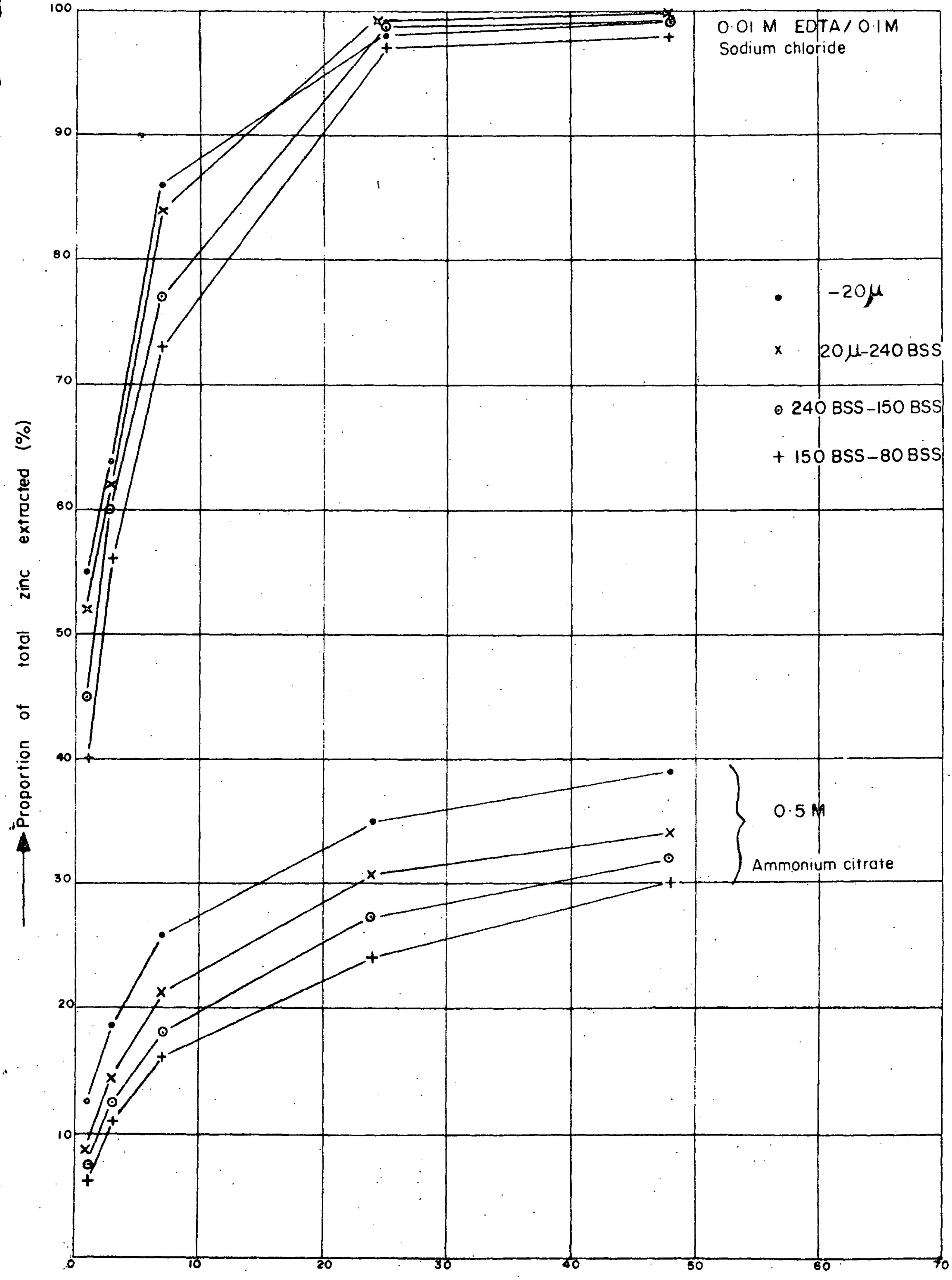

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Fig 9 Extraction of zinc from Sample B using different concentrations of the extractant. Analyses were carried out on the undried sample.

TABLE 3. AMOUNT OF COPPER EXTRACTED AT EQUILIBRIUM FROM THE SIZE FRACTIONS OF SAMPLE A

Extractant	80-120 B.S.S.		120-200 B.S.S.		200 B.S.S. - 20μ		-20μ	
	Extracted Cu (ppm)	Proportion of Total Cu (%)	Extracted Cu (ppm)	Proportion of Total Cu (%)	Extracted Cu (ppm)	Proportion of Total Cu (%)	Extracted Cu (ppm)	Proportion of Total Cu (%)
0.1 M Hydrochloric acid	550	50.6	500	48.6	400	49.6	820	77.9
0.25 M EDTA	500	46.0	420	40.7	380	47.1	800	76.1
0.5 M Ammonium citrate	350	32.2	300	29.1	270	33.5	630	59.9
0.5 M Sodium tartrate	120	11.0	120	11.7	100	12.4	200	19.0
1.0 M Ammonium acetate	60	5.5	47	4.6	30	3.7	90	8.6
1.0 M Ammonium chloride	32	2.9	28	2.7	14	1.7	125	11.9
1.0 M Sodium perchlorate	-10	-0.9	11	1.1	-10	-1.2	14	1.3
1.0 M Sodium chloride	11	1.0	12	1.1	-10	-1.2	14	1.3
Distilled water	-10	-0.9	-10	-1.0	-10	-1.2	-10	-1.0

Footnote: Negative symbol (-) before value indicates "less than" in this and subsequent tables.

TABLE 4. AMOUNT OF ZINC EXTRACTED AT EQUILIBRIUM FROM THE SIZE FRACTIONS OF SAMPLE A

Extractant	80-120 B.S.S.		120-200 B.S.S.		200 B.S.S. - 20 μ		-20 μ	
	Extracted Zn (ppm)	Proportion of Total Zn (%)	Extraction Zn (ppm)	Proportion of Total Zn (%)	Extracted Zn (ppm)	Proportion of Total Zn (%)	Extracted Zn (ppm)	Proportion of Total Zn (%)
0.1 M Hydrochloric acid	345	60.4	325	58.5	340	61.9	410	65.6
0.25 M EDTA	285	49.9	290	52.2	300	54.6	380	60.8
0.5 M Ammonium citrate	175	30.6	200	36.0	200	36.4	265	42.4
0.5 M Sodium tartrate	30*	5.3	20	3.6	50*	9.1	70*	11.2
1.0 M Ammonium acetate	40*	7.0	35	6.3	40	7.3	50*	8.0
1.0 M Ammonium chloride	15	2.6	-10	-1.8	-10	-1.8	20	3.2
1.0 M Sodium perchlorate	-10	-1.8	-10	-1.8	-10	-1.8	-10	-1.6
1.0 M Sodium chloride	-10	-1.8	-10	-1.8	-10	-1.8	-10	-1.6
Distilled water	-10	-1.8	-10	-1.8	-10	-1.8	-10	-1.6

* Equilibrium conditions were not achieved at the conclusion of the experiment.

TABLE 5. AMOUNT OF ZINC EXTRACTED AT EQUILIBRIUM FROM THE SIZE FRACTIONS OF SAMPLE B

Extractant	80-120 B.S.S.		120-200 B.S.S.		200 B.S.S. - 20μ		-20μ	
	Extracted Zn (ppm)	Proportion of Total Zn (%)	Extraction Zn (ppm)	Proportion of Total Zn (%)	Extracted Zn (ppm)	Proportion of Total Zn (%)	Extracted Zn (ppm)	Proportion of Total Zn (%)
0.1 M Hyrochloric acid	1050	78.6	1050	64.4	1230	91.0	1450	87.9
0.25 M EDTA	1000	75.0	1150	70.5	1050	77.7	1450	87.9
0.5 M Ammonium citrate	285	21.3	310	19.0	330	24.4	570	34.6
0.5 M Sodium tartrate	140*	10.5	200*	12.3	250*	18.5	450*	27.3
1.0 M Ammonium acetate	50	3.7	50	3.1	54	4.0	100	6.1
1.0 M Ammonium chloride	70	5.2	57	3.5	92	6.8	150	9.1
1.0 M Sodium perchlorate	11	0.8	12	0.7	20*	1.5	50	3.0
1.0 M Sodium chloride	12	0.9	15	0.9	30*	2.2	50	3.0
Distilled water	-10	-0.8	-10	-0.6	-10	-0.7	-10	-0.6

* Equlibrium conditions were not achieved at the conclusion of the experiment.

(2) Effect of extractant concentration on cxMe values

The equilibrium established between a solid material (MeX) and a ligand (C^{3-}) capable of forming a complex with Me may be represented as follows:

$$\mathrm{Me\,X} + C^{3-} \rightleftharpoons \mathrm{Me\,C}^{-} + X^{2-}$$

where X is SO_4, CO_3, S etc.

The equilibrium constant K may then be written

$$K = \frac{[\mathrm{Me\,C}^{-}]\ [X^{2-}]}{[C^{3-}]}$$

where [ ] denotes activities and [MeX] is, by convention, unity.

$$\therefore\ [\mathrm{Me\,C}^{-}] = K.\ \frac{[C^{3-}]}{[X^{2-}]}$$

In other words, the extraction of a metal depends on the ratio of the activity of the ligand of the extractant and the activity of the displaced anion. In most cases of cold extraction, $[C^{3-}]$ is very much greater than $[X^{2-}]$, and it seemed worthwhile to investigate the effect of varying the concentration of extractant on the cxMe value obtained. To do this, the four fractions of samples A and B were used, and the amounts of copper and zinc extracted after a certain time interval were determined.

Two grams of air-dried sample and 40 ml of extractant were used in all cases, the solutions being shaken and analysed as described earlier. The extraction values obtained at various times for each extractant concentration are shown in Tables 6-13. Not all of these are shown graphically but Figures 10, 11, and 12 illustrate typical results for copper and zinc extraction.

The important point to note from these results is that the amount of reagent commonly used for cold extractable metals is grossly extravagent. For example, 10 percent ammonium citrate is commonly used, but 1 percent and even less is sufficient. For the EDTA extraction, a 25-fold reduction in concentration makes very litle difference to the extraction values. This is understandable when one considers the high stability of the copper and zinc complexes with EDTA. Provided there is an excess of EDTA over the EDTA equivalent of metal, one would expect virtually the same equilibrium position over a very wide concentration range. For example, 2 g of a sample that contains 1000 ppm copper or zinc would need about 16 ml of

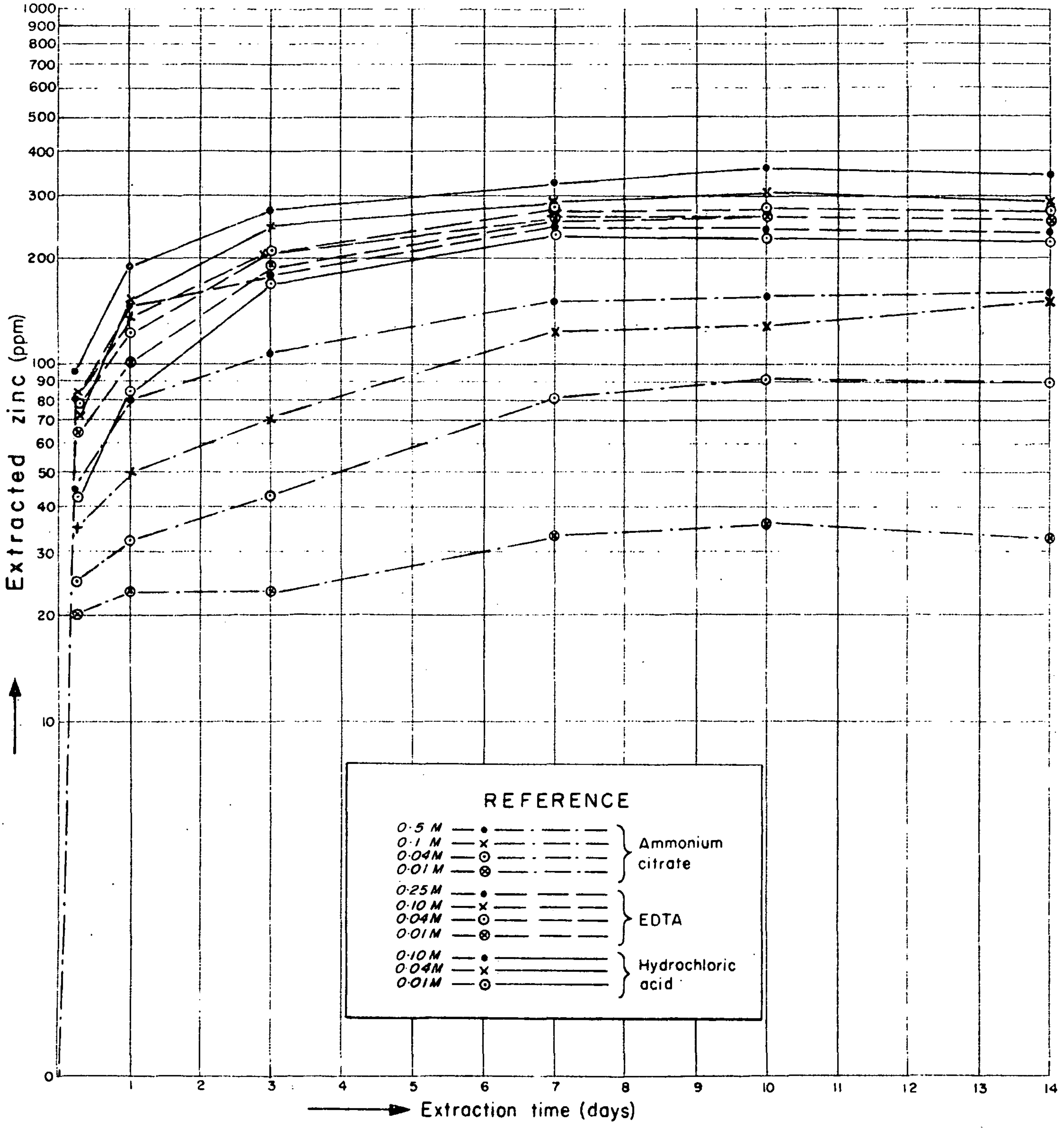

Fig 10 Extraction of zinc from the 80–120 BSS fraction of Sample A

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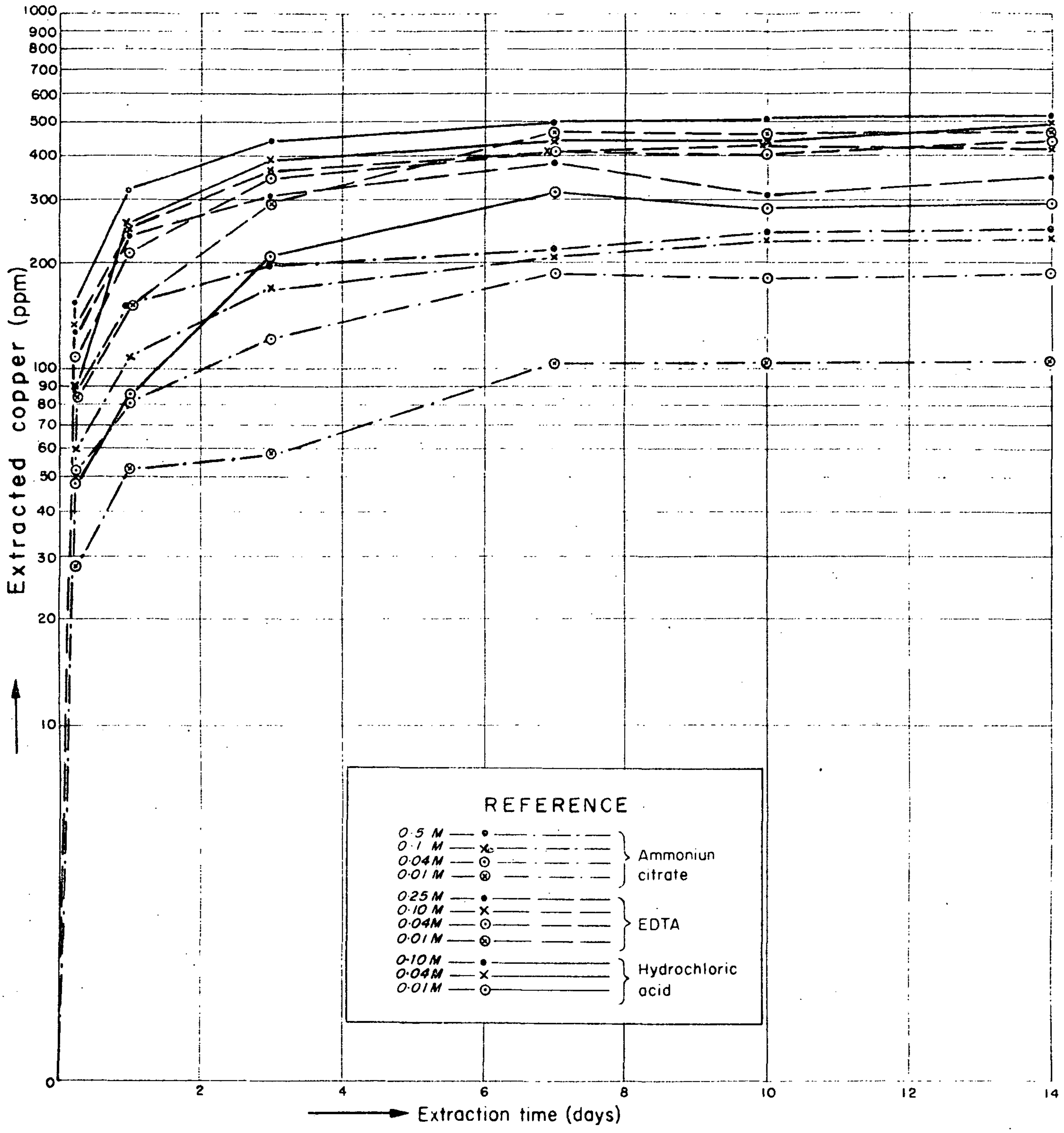

Fig.11. Extraction of copper from the 80–120 B.S.S fraction of sample A

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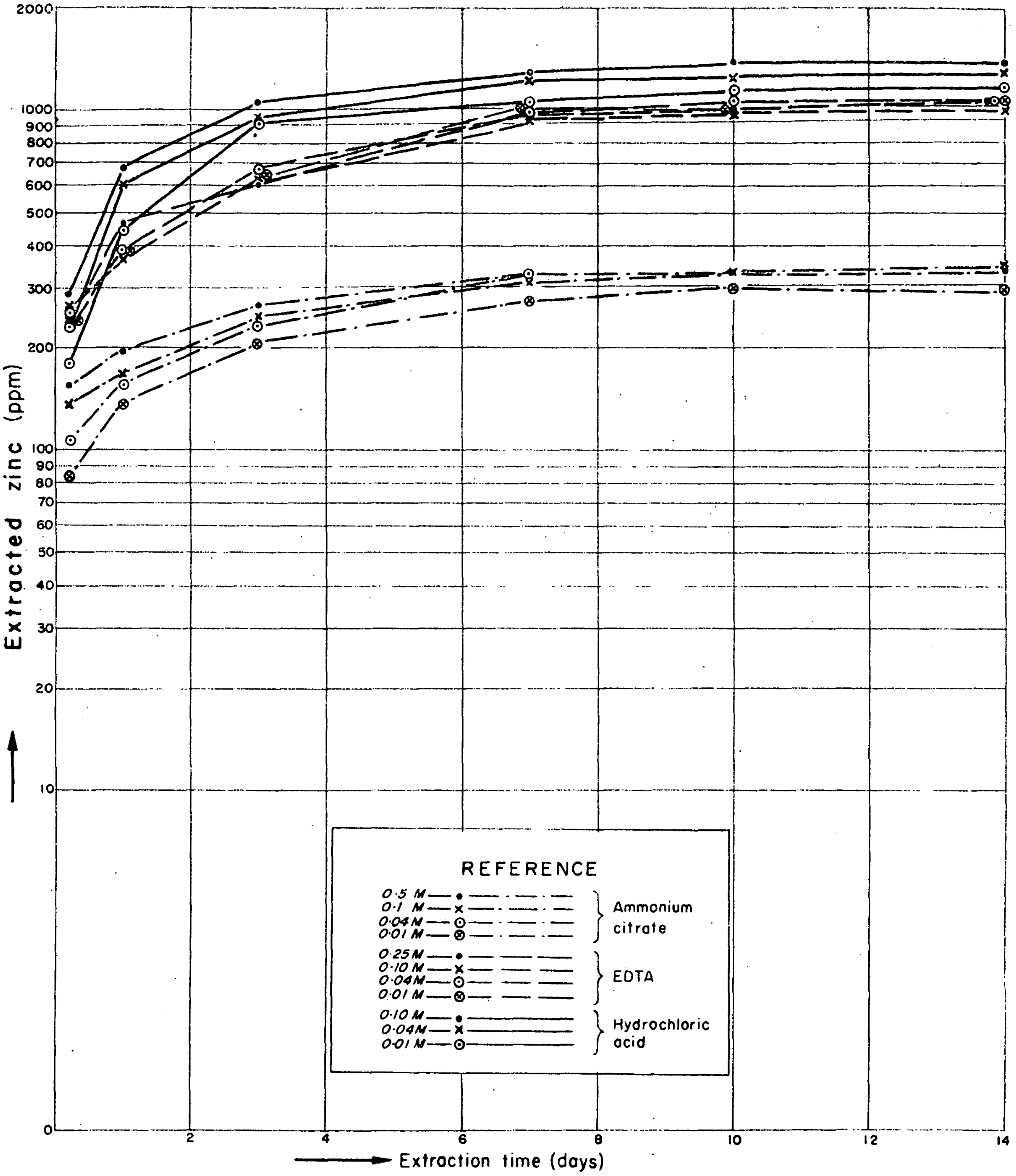

Fig. 12 Extraction of zinc from the −20μ fraction of sample B

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0.01 M EDTA to extract completely the 2000 μ g of the metal. For zinc extraction in both samples and copper extraction in sample A, reducing the EDTA concentration from 0.25 M to 0.01 M affects only very slightly the equilibrium extraction position. The equilibrium position changes much more for both copper and zinc in sample A when the ammonium citrate concentration is reduced. However, the equilibrium extraction position for zinc in sample B changes very little for the same reduction in ammonium citrate concentration. This may be due to the different form of the metals in the two samples, or to the presence (in sample A) of much larger amounts of iron whose strong complexes with citrate would form at the expense of those of copper or zinc.

The only unsatisfactory feature of using dilute solutions of extractants is that they have very little flocculating power and centrifuging is required before analysis. To overcome this difficulty, a mixture containing 0.01 M EDTA and 0.1 M sodium chloride was used; it was found to have excellent extraction powers and in addition, it caused the suspended material to settle quickly. This mixture was used in some later experiments, and in one of the experiments described previously.

(3) Effect of drying out the sample on cxMe values

It is not always possible to collect a wet stream sediment sample for all of any one year. Many workers interested in the geochemical survey programs have expressed doubt as to the validity of cxMe values on stream sediment samples that have been allowed either to dry out in the laboratory before analysis or have been dried naturally in the creek and river beds. This section of the work was designed to investigate this matter.

Two new samples A and B from the same sources as the original samples, were collected and separated into four size fractions as previously described. Each size fraction from each sample was divided into three roughly equal parts. The first part was kept under distilled water, the second part was dried out at 40°C, and the third part was dried out at 100°C. The second and third parts were kept in their respective ovens at these temperatures even after they had dried out, and samples for the experimental work were taken from them when required. There was, therefore, some attempt to accelerate any 'ageing' of the sediments by using prolonged and elevated temperatures.

Ammonium citrate (0.5 M) was used because when this phase of the work was started, it was considered to be the most suitable extractant available, and the results of the earlier work were not known at the time. If the 'ageing' process did affect the cxMe value it was assumed that it

TABLE 6. EXTRACTION OF COPPER AND ZINC FROM THE 80 - 120 B.S.S. FRACTION OF SAMPLE A

	Extraction Time (days)											
	1/4		1		3		7		10		14	
Extractant	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
0.5 M Ammonium citrate	88	46	156	80	198	108	220	150	244	153	251	158
0.1 M Ammonium citrate	64	35	108	49	170	70	210	122	232	127	230	150
0.04 M Ammonium citrate	52	25	80	32	122	43	186	80	180	92	185	52
0.01 M Ammonium citrate	38	20	52	23	58	23	103	33	103	36	106	33
0.25 M EDTA	128	82	236	148	308	178	382	241	310	240	342	234
0.1 M EDTA	132	82	250	136	356	206	410	258	430	260	422	273
0.04 M EDTA	108	78	212	120	346	202	402	268	404	272	428	253
0.01 M EDTA	84	65	154	100	298	187	462	256	458	272	458	253
0.1 M Hydrochloric acid	152	96	320	188	444	270	490	321	514	357	520	344
0.04 M Hydrochloric acid	88	74	244	150	384	245	435	285	425	302	450	280
0.01 M Hydrochloric acid	48	43	82	84	208	168	312	233	284	230	295	222

Note: All results in ppm

TABLE 7. EXTRACTION OF COPPER AND ZINC FROM THE 120 - 200 B.S.S. FRACTION OF SAMPLE A

	Extraction Time (days)											
	1/4		1		3		7		10		14	
Extractant	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
0.5 M Ammonium citrate	88	52	142	88	180	112	197	151	220	153	220	163
0.1 M Ammonium citrate	64	36	90	51	140	70	180	113	184	118	190	140
0.04 M Ammonium citrate	54	30	76	38	96	46	150	74	143	77	158	88
0.01 M Ammonium citrate	36	26	48	26	50	26	79	28	77	30	62	38
0.25 M EDTA	120	84	186	120	288	178	362	241	218	240	318	233
0.1 M EDTA	122	84	216	120	316	196	416	250	364	260	374	240
0.04 M EDTA	112	84	206	126	346	210	438	268	403	270	422	247
0.01 M EDTA	96	74	160	88	288	182	428	250	430	270	422	252
0.1 M Hydrochloric acid	168	110	308	196	412	272	500	312	480	334	472	320
0.04 M Hydrochloric acid	100	87	230	106	336	245	405	285	404	292	395	280
0.01 M Hydrochloric acid	48	54	70	80	150	150	217	217	190	210	190	208

Note: All results in ppm

TABLE 8. EXTRACTION OF COPPER AND ZINC FROM THE 200 B.S.S. - 20 FRACTION OF SAMPLE A

	Extraction Time (days)											
	1/4		1		3		7		10		14	
Extractant	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
0.5 M Ammonium citrate	104	72	132	106	152	124	155	166	174	163	176	177
0.1 M Ammonium citrate	80	60	100	76	122	92	147	143	148	140	152	163
0.04 M Ammonium citrate	74	49	90	59	102	70	132	100	121	100	132	112
0.01 M Ammonium citrate	56	86	64	38	60	38	79	49	70	52	76	57
0.25 M EDTA	132	112	180	146	250	196	312	250	244	250	270	240
0.1 M EDTA	136	116	204	156	274	212	351	268	298	292	318	260
0.04 M EDTA	142	108	212	146	298	226	382	277	350	292	356	266
0.01 M EDTA	132	108	192	138	282	216	366	277	364	292	356	266
0.1 M Hydrochloric acid	165	126	258	203	346	282	340	380	400	323	388	326
0.04 M Hydrochloric acid	120	102	198	160	270	240	325	294	324	292	306	280
0.01 M Hydrochloric acid	60	80	92	111	132	178	168	232	142	220	140	220

Note: All results in ppm

TABLE 9. EXTRACTION OF COPPER AND ZINC FROM THE -20 FRACTION OF SAMPLE A

	Extraction Time (days)											
	1/4		1		3		7		10		14	
Extractant	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
0.5 M Ammonium citrate	292	116	320	143	388	173	382	224	430	210	414	220
0.1 M Ammonium citrate	294	102	316	116	378	138	428	190	418	192	400	196
0.04 M Ammonium citrate	316	96	302	94	358	100	416	143	390	136	368	148
0.01 M Ammonium citrate	240	72	232	69	282	68	331	94	330	100	286	100
0.25 M EDTA*												
0.1 M EDTA*												
0.04 M EDTA*												
0.01 M EDTA*												
0.1 M Hydrochloric acid	420	174	500	274	560	363	740	414	688	420	720	410
0.04 M Hydrochloric acid	324	142	448	262	445	318	610	380	570	382	572	360
0.01 M Hydrochloric acid	148	96	174	166	182	187	210	241	175	232	167	220

Note: All results in ppm

* Insufficient material for the EDTA extractions

TABLE 10. EXTRACTION OF ZINC FROM 80 - 120 B.S.S. FRACTION OF SAMPLE B

	Extraction Time (days)					
Extractant	1/4	1	3	7	10	14
0.5 M Ammonium citrate	50	76	93	128	136	150
0.1 M Ammonium citrate	49	68	80	128	128	150
0.04 M Ammonium citrate	41	51	67	100	110	122
0.01 M Ammonium citrate	36	49	58	88	84	100
0.25 M EDTA	74	144	235	350	369	377
0.1 M EDTA	74	160	286	390	334	422
0.04 M EDTA	78	196	297	402	462	422
0.01 M EDTA	95	200	315	414	462	434
0.1 M Hydrochloric acid	110	316	562	790	810	890
0.04 M Hydrochloric acid	80	246	463	670	765	750
0.01 M Hydrochloric acid	54	160	388	544	583	660

Note: All results in ppm

TABLE 11. EXTRACTION OF ZINC FROM THE 120 - 200 B.S.S. FRACTION OF SAMPLE B

	Extraction Time (days)					
Extractant	1/4	1	3	7	10	14
0.5 M Ammonium citrate	65	97	120	167	172	190
0.1 M Ammonium citrate	58	78	105	150	158	190
0.04 M Ammonium citrate	51	66	82	128	144	158
0.01 M Ammonium citrate	39	52	69	100	108	132
0.25 M EDTA	82	188	318	479	520	530
0.1 M EDTA	87	202	346	510	568	550
0.04 M EDTA	87	210	375	526	582	568
0.01 M EDTA	90	240	387	526	568	530
0.1 M Hydrochloric acid	132	380	653	1000	1050	1020
0.04 M Hydrochloric acid	96	300	538	790	860	885
0.01 M Hydrochloric acid	68	202	445	620	650	750

Note: All results in ppm

TABLE 12. EXTRACTION OF ZINC FROM THE 200 B.S.S. - 20 FRACTION OF SAMPLE B

	Extraction Time (days)					
Extractant	1/4	1	3	7	10	14
0.5 M Ammonium citrate	72	112	133	174	181	197
0.1 M Ammonium citrate	70	87	120	174	172	190
0.04 M Ammonium citrate	65	80	100	158	162	177
0.01 M Ammonium citrate	54	67	82	129	144	158
0.25 M EDTA	102	240	329	450	490	473
0.1 M EDTA	106	194	335	480	550	562
0.04 M EDTA	96	194	350	510	568	532
0.01 M EDTA	116	194	363	510	550	542
0.1 M Hydrochloric acid	143	380	628	915	960	910
0.04 M Hydrochloric acid	126	317	522	755	869	850
0.01 M Hydrochloric acid	68	224	432	620	633	730

Note: All results in ppm

TABLE 13. EXTRACTION OF ZINC FROM THE - 20 FRACTION OF SAMPLE B

	Extraction Time (days)					
Extractant	1/4	1	3	7	10	14
0.5 M Ammonium citrate	155	196	266	330	334	335
0.1 M Ammonium citrate	137	168	245	312	334	345
0.04 M Ammonium citrate	108	155	235	322	337	345
0.01 M Ammonium citrate	85	137	205	277	300	292
0.25 M EDTA	264	462	618	995	1000	1040
0.1 M EDTA	262	362	618	950	1000	980
0.04 M EDTA	233	392	672	995	1050	1040
0.01 M EDTA	246	377	653	1040	1050	1040
0.1 M Hydrochloric acid	290	670	1044	1290	1355	1330
0.04 M Hydrochloric acid	238	600	956	1210	1250	1260
0.01 M Hydrochloric acid	180	462	928	1035	1150	1175

Note: All results in ppm

would affect cxMe values for other extractants, not necessarily identically, but certainly similarly. Samples for extraction were taken after 1, 2, 6, and 14 days drying at their respective temperatures. Two grams of stream sediment and 40 ml of extractant were taken in every case; the analyses were made after shaking for the times shown in Tables 14-16, and in Figures 13-18. The latter refer only to the 80-120 B.S.S. size fractions; results for other size fractions are not shown graphically.

The results indicate that the drying out of a sample affects the rate at which the equilibrium position is reached and possibly the equilibrium value of cxMe. The higher the temperature of drying the slower the extraction rate. Indeed, for all size fractions of sample B, equilibrium was not achieved after 20 days extraction. High temperature of drying and a long period of drying both reduce the cxMe value below that obtained on the undried material under otherwise identical conditions. It is not easy to decide whether this is important from a geochemical prospecting point of view. Certainly, on the two samples used in this study, the lower cxMe values obtained on drying out would not have prevented the detection of the large amount of copper and/or zinc in the samples. It is difficult to say whether samples that contain a lower total content of copper or zinc would have been affected more drastically by 'ageing'. What is clear, however, is that 'ageing' of samples by drying out and subjecting them to elevated temperatures, affects different samples differently. For example, the cxZn value for sample B was more seriously affected by 'ageing' than that of sample A. This could conceivably give misleading or false anomalies. It should be stressed that cxMe values obtained at other than equilibrium conditions are not strictly comparable and care should be exercised when doing so. However, this may not detract from their usefulness in geochemical prospecting, providing one bears in mind that reaction rates and 'ageing' of samples play a big part in cxMe values obtained and one makes allowances accordingly, particularly with regard to so-called 'subtle' anomalies.

The reason the 'ageing' process affects the cxMe value is probably that the chemical precipitates form aggregates and distinct crystals under these conditions. If the cxMe value is due to sorption of metal ions or compounds on, for example, clay minerals, metal ions from the surface of the clay may migrate to sites within the lattice as suggested by Elgabaly (1950).

It should be emphasized that the results refer to stream sediment samples in only two types of terrain and similar results might not be obtained in other areas.

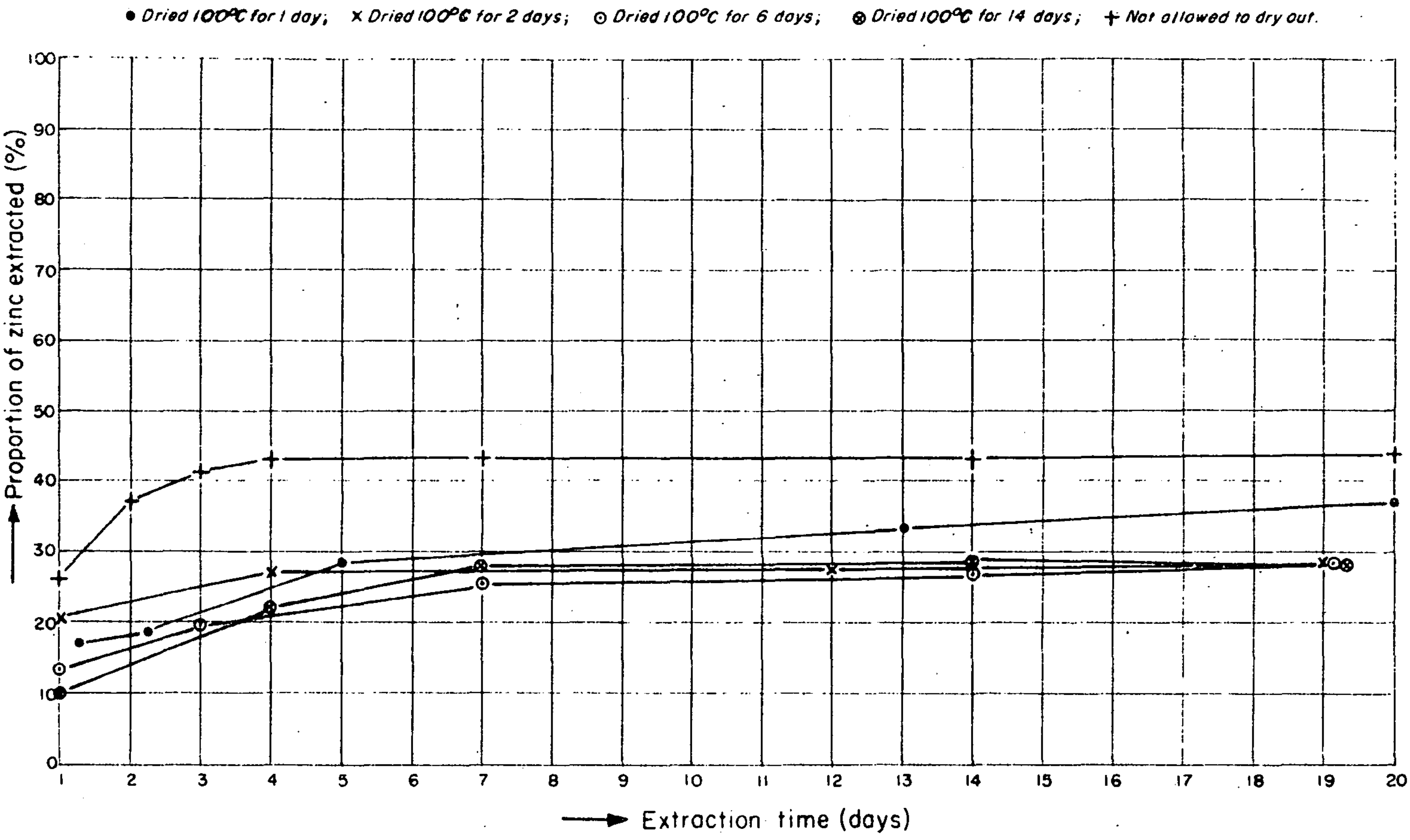
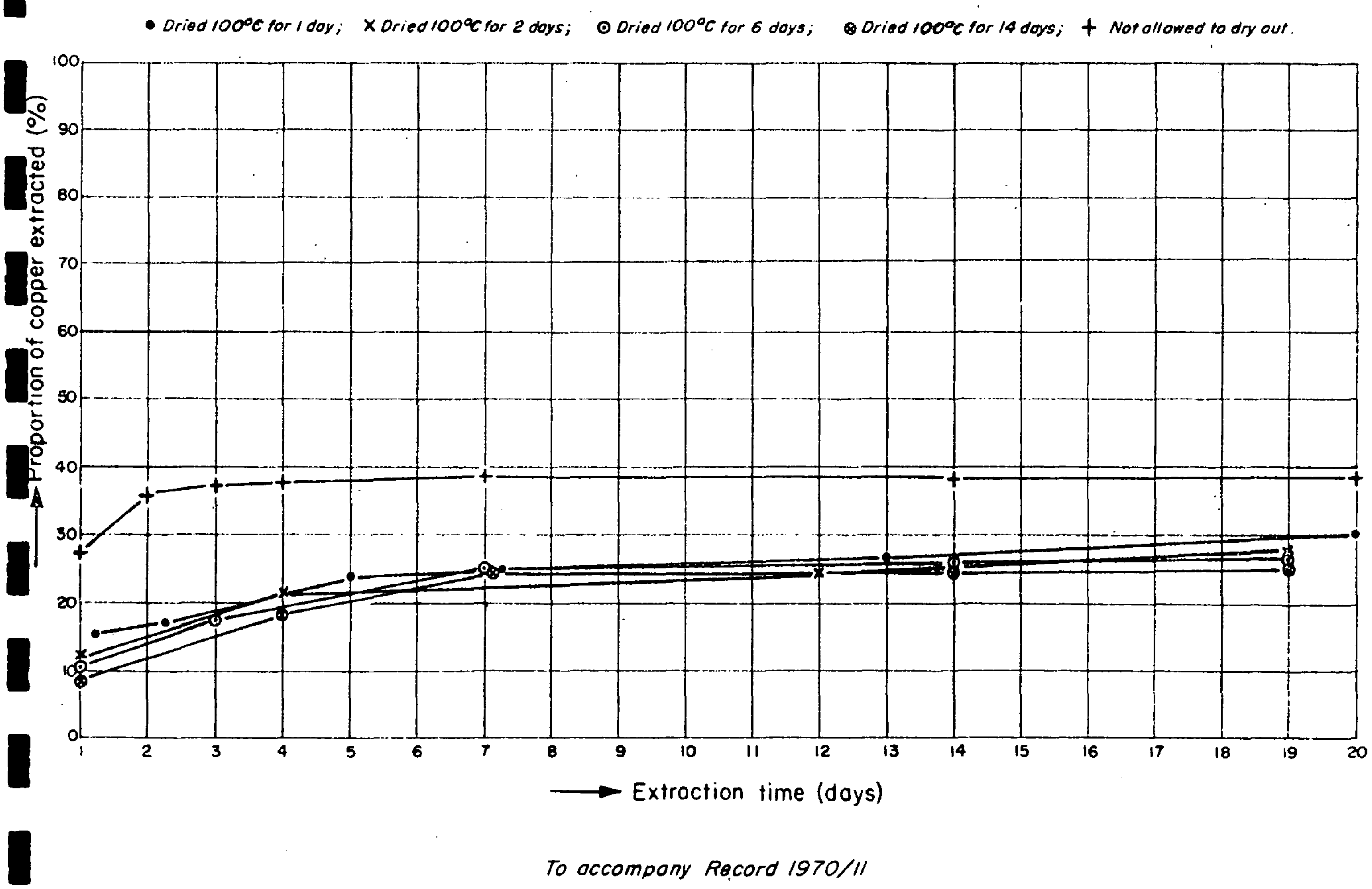


Fig 13 Extraction of zinc by 0·5M ammonium citrate from the 80-120 B.S.S. fraction of sample A dried at 100°C



To accompany Record 1970/11

Fig. 14. Extraction of copper by 0·5M ammonium citrate from the 80-120 B.S.S. fraction of sample A dried at 100°C

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M(G)50

TABLE 14. EXTRACTION OF COPPER FROM SAMPLE A USING 0.5 M AMMONIUM CITRATE

Drying Time (days)	Extraction Time (days)	Size Fraction 80-120 B.S.S.		10-200 B.S.S.		200 B.S.S. - 20µ		-20µ	
		Percentage Extraction at 40°C and 100°C							
		40°C	100°C	40°C	100°C	40°C	100°C	40°C	100°C
	1 1/4	13.4	15.5	14.7	12.6	20.4	17.8	31.3	36.2
	2 1 4	13.6	17.0	17.9	13.2	22.4	19.4	35.2	39.4
	5	27.2	23.8	26.4	19.7	29.6	25.7	47.2	43.2
	13	34.7	26.2	33.3	26.4	34.2	32.6	52.3	52.2
	20	37.0	30.1	34.2	26.5	34.7	32.9	55.7	56.2
	1	13.6	11.7	14.8	11.8	18.9	15.2	34.7	31.0
	4	22.7	21.4	23.7	20.6	26.0	21.4	52.7	48.5
	12	30.2	24.3	32.5	28.4	32.8	29.5	55.8	47.5
	19	32.3	28.0	31.7	27.7	35.1	29.2	61.8	56.4
6	1	12.0	10.5	12.0	10.1	17.1	14.1	33.2	31.1
	3	21.2	17.6	17.5	15.0	21.5	21.3	45.3	39.8
	7	29.0	24.2	25.7	20.6	32.0	26.7	56.0	45.8
	14	29.2	25.3	26.8	22.5	34.5	26.7	58.2	49.1
	19	29.5	26.8	27.9	23.5	34.7	27.1	60.8	50.9
14	1	9.4	8.9	10.3	8.9	13.9	11.6	29.4	29.7
	4	12.8	18.4	20.4	14.3	23.1	19.5	51.0	38.0
	7	18.7	24.9	24.4	17.3	27.8	22.7	57.0	41.8
	14	23.3	24.9	25.2	18.5	30.5	24.5	59.2	43.7
	19	24.5	25.5	26.0	19.8	31.7	25.3	59.5	44.7
Wet Sample	1	27.2		21.0		24.7		41.7	
	2	35.6		20.9		27.5		52.8	
	3	37.1		33.1		33.6		62.1	
	4	37.7		34.2		36.0		63.1	
	7	38.7		33.9		36.0		64.0	
	14	38.5		34.5		36.5		64.0	
	20	38.9		34.8		36.7		65.0	

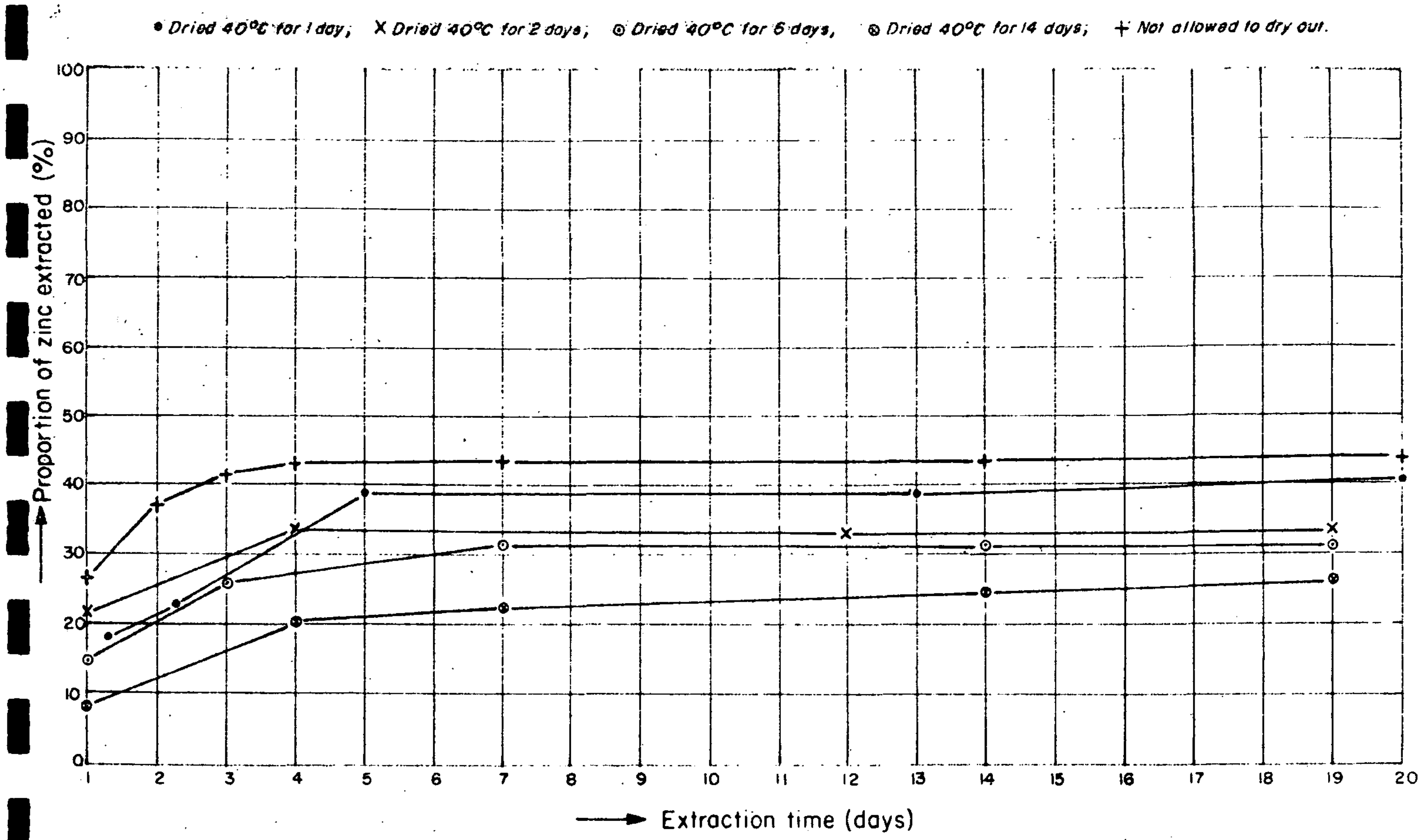
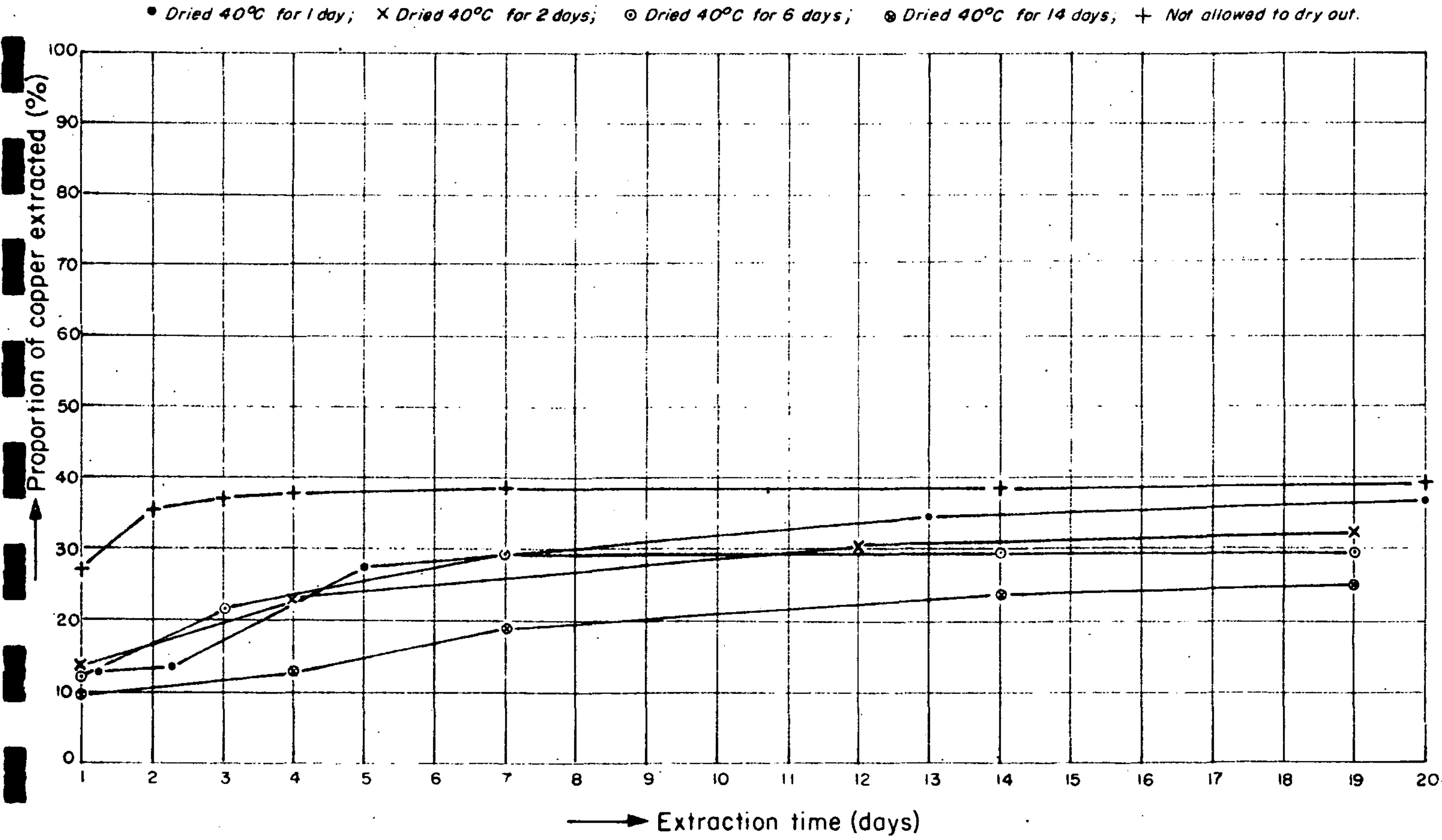


Fig. 15. Extraction of zinc by 0·5M ammonium citrate from the 80-120 B.S.S. fraction of sample A dried at 40°C



To accompany Record 1970/11

M (G) 51.

Fig.16. Extraction of copper by 0·5M ammonium citrate from the 80-120 B.S.S. fraction of sample A dried at 40°C

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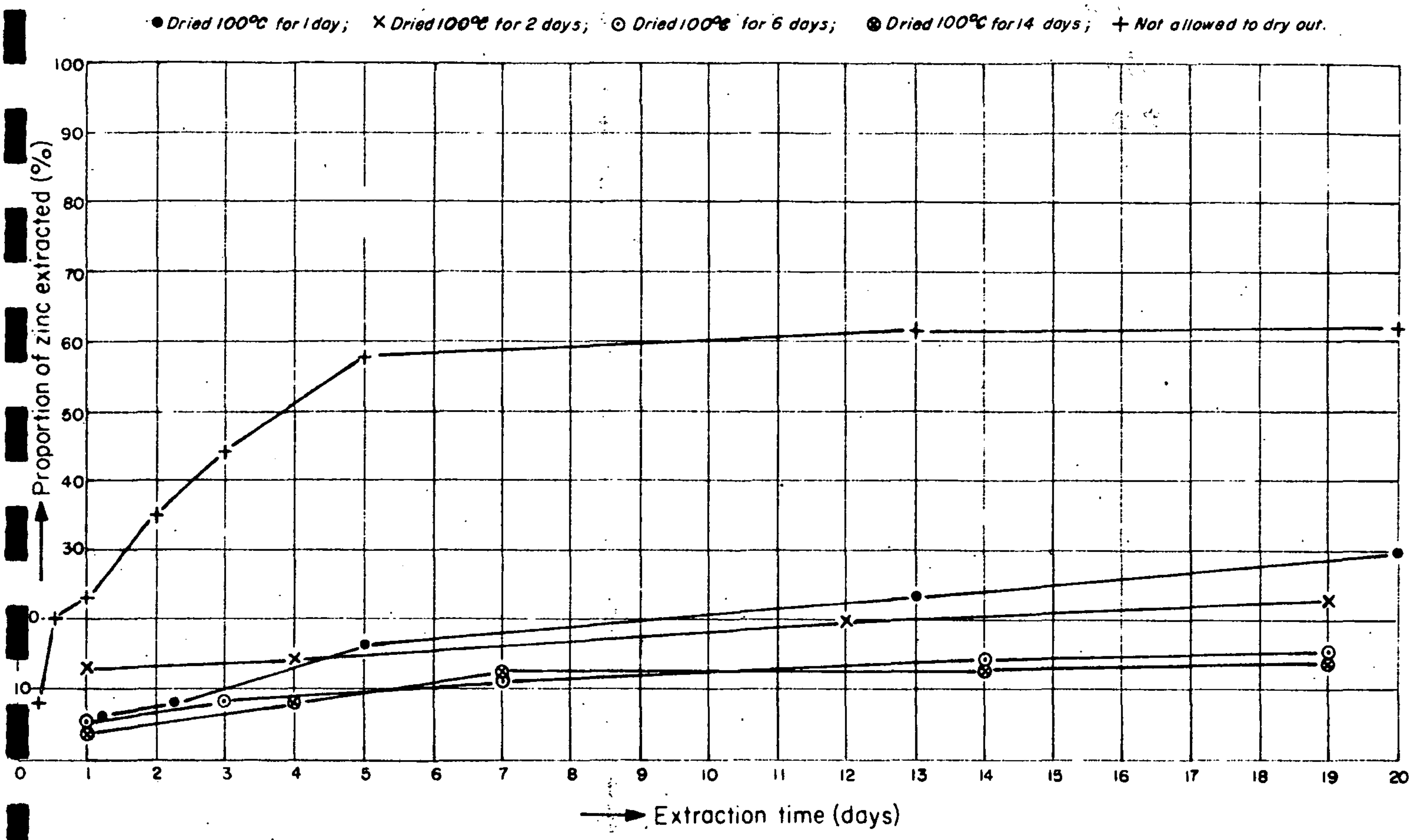
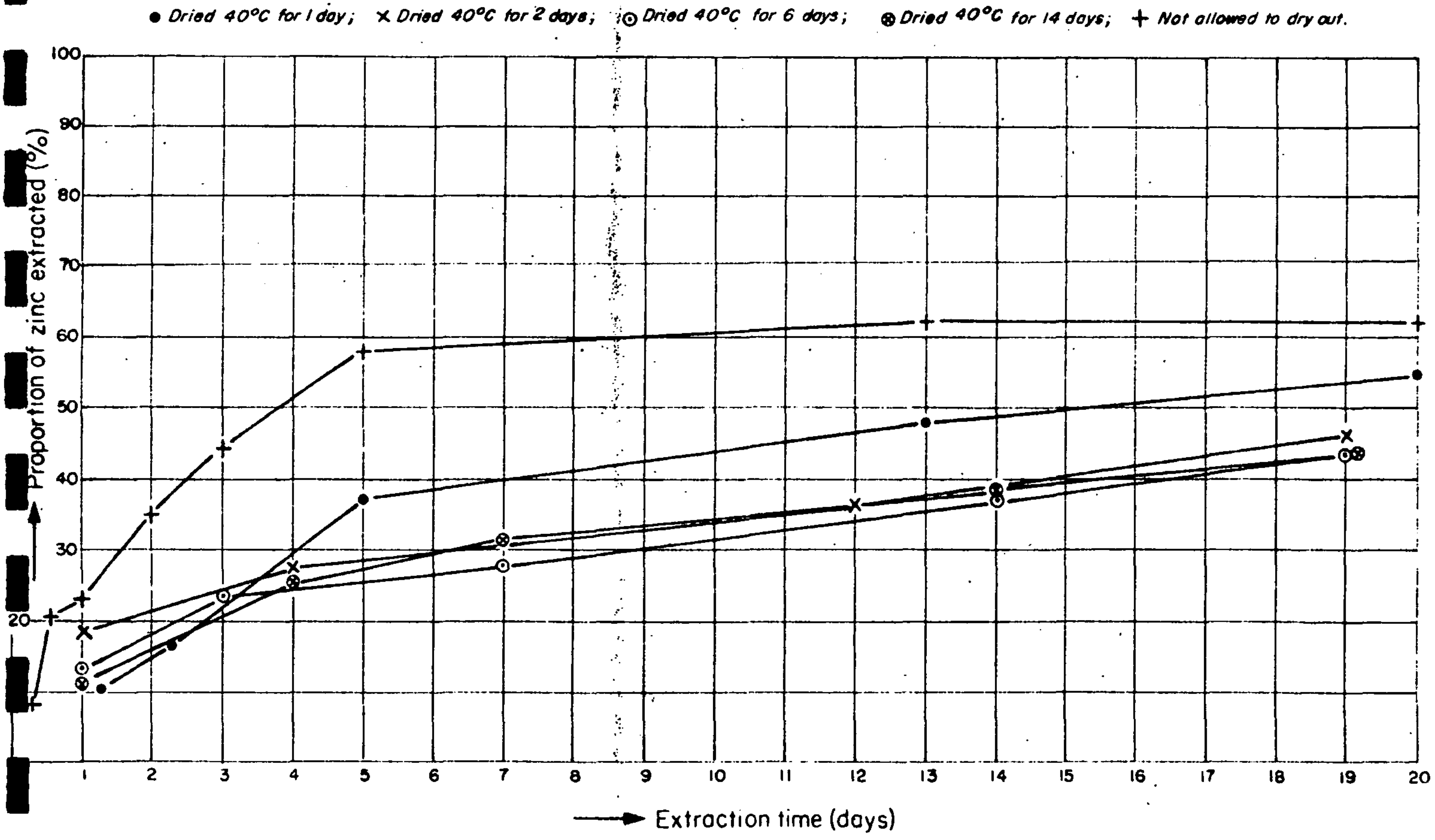


Fig. 17. Extraction of zinc by 0·5M ammonium citrate from the 80-120 B.S.S. fraction of sample B dried at 100°C



To accompany Record 1970/11

M (G) 52

Fig. 18. Extraction of zinc by 0·5M ammonium citrate from the 80-120 B.S.S. fraction of sample B dried at 40°C

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TABLE 15. EXTRACTION OF ZINC FROM SAMPLE A USING 0.5 M AMMONIUM CITRATE

Drying Time (days)	Extraction Time (days)	Size Fraction							
		80-120 B.S.S.		10-200 B.S.S.		200 B.S.S. - 20μ		-20μ	
		Percentage Extraction at 40°C and 100°C							
		40°C	100°C	40°C	100°C	40°C	100°C	40°C	100°C
1	1 1/4	18.0	17.2	21.1	16.7	20.7	16.8	26.8	25.4
	2 1/4	22.8	18.8	25.5	18.0	23.2	21.5	31.0	27.7
	5	38.8	28.8	33.8	30.3	26.4	28.6	44.8	41.7
	13	38.8	33.6	40.0	32.9	34.6	30.7	45.0	42.8
	20	40.5	37.3	39.5	38.0	36.4	31.1	45.5	49.3
2	1	21.6	20.8	28.1	21.1	22.1	15.4	21.6	22.7
	4	33.7	27.3	37.3	32.5	23.2	27.2	46.6	39.3
	12	33.2	28.0	36.4	29.5	32.2	27.8	47.0	39.3
	19	33.7	28.8	35.5	31.2	35.0	28.3	47.0	39.3
6	1	14.8	13.6	15.5	12.3	17.0	12.9	18.9	16.3
	3	25.6	20.0	24.6	18.4	22.8	19.5	30.3	25.8
	7	31.2	25.7	30.8	22.0	27.8	23.5	39.3	30.3
	14	31.1	27.3	30.4	24.1	29.3	23.5	41.7	34.2
	19	30.8	28.5	30.7	25.5	30.7	25.0	44.0	36.7
14	1	8.5	10.4	11.8	9.5	13.3	10.0	15.1	14.4
	4	20.0	22.5	21.0	15.8	21.0	19.5	27.6	27.3
	7	22.4	28.0	30.8	24.0	27.8	23.6	37.1	34.0
	14	24.8	28.0	31.8	24.1	28.5	25.7	39.4	34.8
	19	26.4	28.0	30.7	27.2	28.5	27.0	40.9	36.7
Wet Samples	1	26.8		27.8		25.0		39.6	
	2	37.3		36.0		30.7		45.0	
	3	41.4		39.6		34.3		49.0	
	4	43.2		43.0		36.5		50.8	
	7	43.7		43.9		36.5		50.2	
	14	43.5		43.5		37.1		51.8	
	20	44.0		43.9		37.8		51.8	

TABLE 16. EXTRACTION OF ZINC FROM SAMPLE B USING 0.5 M AMMONIUM CITRATE

Drying Time (days)	Extraction Time (days)	Size Fraction 80-120 B.S.S.		120-200 B.S.S.		200 B.S.S. - 20µ		-20µ	
		Percentage Extraction at 40°C and 100°C							
		40°C	100°C	40°C	100°C	40°C	100°C	40°C	100°C
1	1 1/4	10.2	6.4	8.9	5.6	12.3	7.1	17.1	11.3
	2 1/4	16.7	8.1	17.4	7.4	19.4	9.5	25.8	14.7
	5	37.3	16.3	39.4	15.2	41.0	17.5	42.6	27.3
	13	47.7	23.1	43.7	21.8	49.2	25.0	45.4	36.0
	20	54.8	30.0	47.8	22.4	53.8	34.7	46.0	40.4
2	1	18.1	13.7	8.8	7.9	9.7	10.2	9.0	9.6
	4	27.5	14.8	26.8	12.1	28.4	15.8	36.0	28.2
	12	36.2	20.0	34.5	17.0	37.3	20.8	45.0	37.8
	19	46.2	23.1	41.8	21.2	47.8	26.8	45.4	40.8
6	1	13.5	5.8	6.7	4.6	8.4	7.1	6.8	7.6
	3	23.1	8.5	17.5	8.5	18.7	13.0	26.5	16.6
	7	27.7	11.6	24.9	12.1	29.8	16.8	38.5	24.8
	14	36.9	14.2	26.8	12.4	31.7	17.5	44.0	25.0
	19	43.2	15.4	27.7	13.5	34.8	18.6	44.6	29.5
14	1	11.6	4.2	6.7	3.0	8.4	3.7	12.4	6.5
	4	25.0	8.5	16.4	6.7	17.5	13.2	24.8	12.7
	7	31.0	12.2	23.6	9.4	26.8	14.6	35.0	25.1
	14	38.5	13.3	25.1	10.2	28.3	15.1	39.5	26.8
	19	43.0	14.0	25.7	10.3	30.7	15.7	40.3	28.5
Wet Sample	1/4	8.0		8.3		11.7		8.0	
	½	20.6		21.8		22.7		14.8	
	1	23.1		26.4		22.7		16.3	
	2	35.0		28.5		28.5		26.7	
	3	44.6		32.2		31.3		35.0	
	5	57.8		47.8		44.4		42.2	
	13	61.8		52.8		56.8		46.0	
	20	62.0		53.0		57.8		46.2	

(4) Influence of primary and secondary minerals on cxMe values

This particular problem became apparent when detrital particles of chalcopyrite, azurite, and malachite were seen in the coarse fraction of the stream sediment sample A. The copper minerals were easily identified by their colour. Because of the proximity of the sampling sites to the orebodies it was reasoned that if primary and secondary copper minerals were found in the stream sediments, it was likely that primary and secondary lead and zinc minerals would be present as these form part of the same orebody. However, these could be hard to identify visually if present in small amounts.

The primary and secondary copper, lead, and zinc minerals listed in Table 17, were collected in as pure a form as possible. The minerals were crushed and sieved through 80 B.S.S., 150 B.S.S., and 240 B.S.S. mesh sieves. All fractions were collected. The - 240 B.S.S. fraction was too variable in grainsize and was not used further in the experiments except for the galena and bornite studies reported in Figures 21 and 22.

In the experiments to study attack on minerals by cold extractants only the two size ranges, 80-150 B.S.S. (180-105μ) and 150-240 B.S.S., (105-65μ) were used. One quarter gram of the two size fractions of each mineral was shaken with 40 ml of 0.5 M ammonium citrate solution for about thirty minutes in a sealed tube, after which time the supernatant liquids were analysed for the major cation. Shaking was continued for seven days except when small aliquots of solution were removed for analysis after three hours, eight hours, one day, three days, and seven days. The results are shown in Figure 19 for the 80-150 B.S.S. size fractions. Results for the finer fractions are not shown here, but are similar to those for the coarser fractions. They differ only in that the initial reaction rate is slightly quicker for the finer fraction. For convenience, the results are expressed as percentage of total metal in the sample fraction.

The experiment was repeated using 0.01 M EDTA/0.1 M sodium chloride as extractant instead of 0.5 M ammonium citrate. The results for the 80-150 B.S.S. fraction are shown in Figure 20. Once again the finer fractions differed only in that the reaction rate was slightly higher, and examples of this are shown in Figures 21 and 22. In compiling the plots shown in Figures 19 and 20 some of the data have been grouped to avoid overcrowding. It can be seen that the breakdown of minerals by ammonium citrate or by 0.01 M EDTA/0.1 M sodium chloride is not a rapid process, as in most cases several days are required before equilibrium conditions are established.

TABLE 17. MINERALS USED IN COLD EXTRACTION STUDIES

Mineral	Formula	Primary (P) or Secondary (S)
Cuprite	Cu_2O	S
Bornite	Cu_5FeS_4	P and S
Chalcopyrite	$CuFeS_2$	P and S
Chrysocolla	$CuSiO_3 . 2H_2O$	S
Azurite	$2CuCO_3 . Cu(OH)_2$	S
Malachite	$CuCO_3 . Cu(OH)_2$	S
Chalcocite	Cu_2S	S
Smithsonite	$ZnCO_3$	S
Hemimorphite	$H_2O . 2ZnO . SiO_2$	S
Sphalerite	ZnS	P
Cerussite	$PbCO_3$	S
Galena	PbS	P
Pyromorphite	$(PbCl)Pb_4(PO_4)_3$	S
Anglesite	$PbSO_4$	S

Indications are that azurite, malachite, and possibly some of the other secondary minerals studied, are completely extracted by 0.5 M ammonium citrate after a few days extraction. Other secondary minerals are not attacked so easily, and the primary minerals, namely the sulphides, are still more resistant, although none are inert. It is possible that a coating of a less inert secondary product is responsible for some of the small reactivity of the sulphides. Equilibrium conditions appear to be established much more quickly using the 0.01 M EDTA/0.1 M sodium chloride reagent, although the equilibrium position occurs with much less metal ion released. This is because the amount of EDTA available for complex formation is limited.

In order to understand the results, we have to realise that for the release of one equivalent of metal ion by complexing with citrate ion or EDTA, there is a simultaneous release of one equivalent of anion, be it carbonate, sulphide, hydroxide, sulphate etc. These anions are released into solution, and although some may escape as a volatile gas (the smell of H_2S could be detected after 6 days extraction of bornite), most of them, including part of the sulphide, form an equilibrium mixture in the solution. The rate of dissolution of the various minerals depends, therefore, on the stability constants of the various minerals, and on the equilibrium constant of the particular metal ion with citrate or EDTA. Considering the solubility product of the various sulphides, it is not suprising that they are only attacked slowly by EDTA and even more slowly by ammonium citrate.

The amount of metals present in cation exchange positions in stream sediments is probably very small. A large proportion of anomalous metal is present as detrital particles of primary or secondary minerals or as direct precipitates of such compounds as sulphates, chlorides, and carbonates which behave as secondary minerals. If this is so, the results shown in Figures 19-22 make it clear why leaching experiments of only two minutes duration can give rise to most irreproducible results, although the anomaly may not necessarily remain undetected.

(5) Relationship between cxMe values and 'total' metal content.

To investigate this problem 253 stream sediment samples (-80 B.S.S. mesh) from a mineralized area near Herberton, north Queensland, were analysed for 'total' copper, lead, and zinc, following an aqua regia digest. After shaking 1 g of each sample with 40 ml of extractant for seven days, virtual equilibrium extraction values were obtained for copper, lead, and zinc for the extractants 0.1 M hydrochloric acid, 0.5 M ammonium citrate, and 0.01 M EDTA/0.1 M sodium chloride.

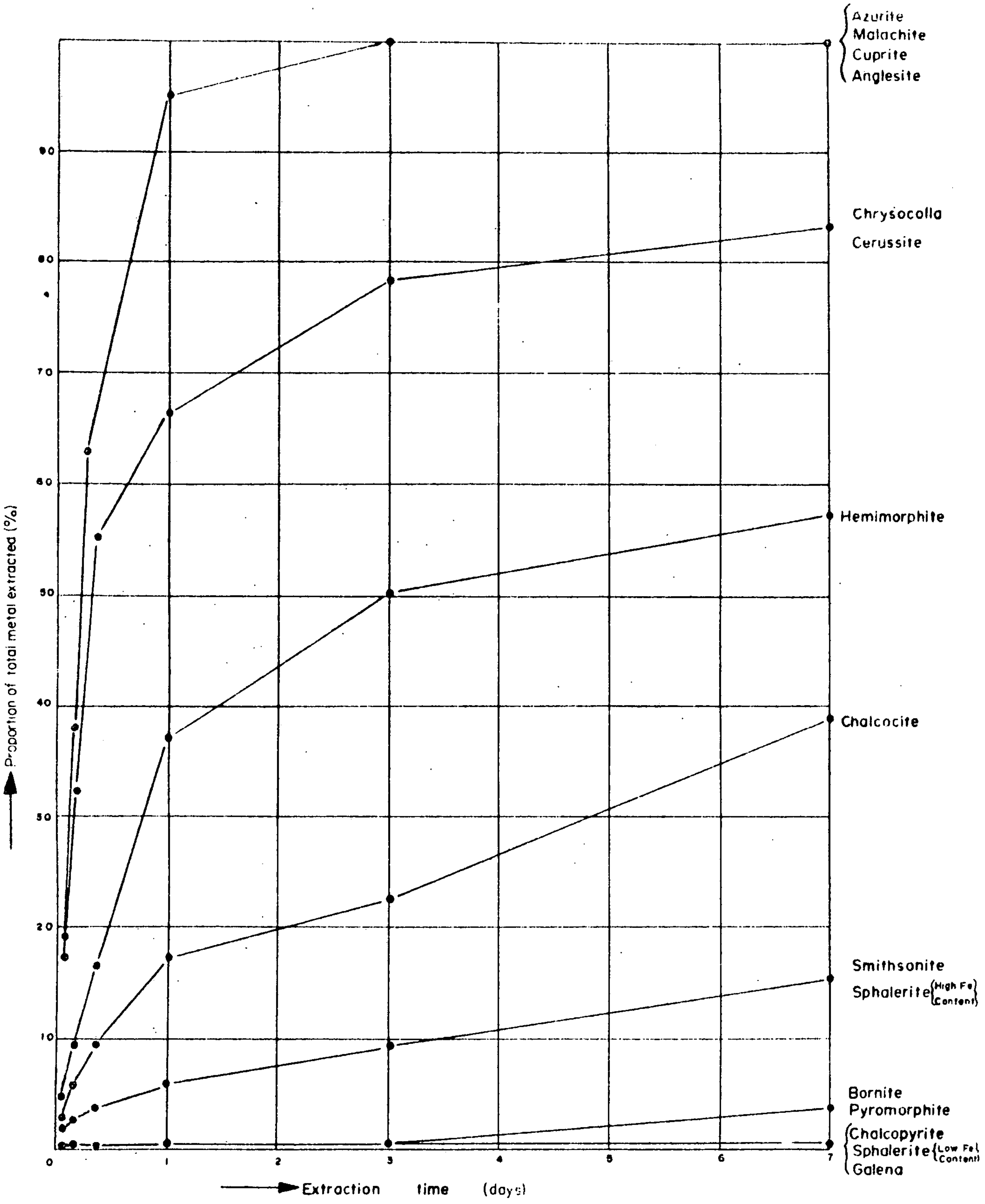
To make the results easier to interpret, the aqua regia 'totals' were arranged in order of increasing magnitude and these are shown plotted in Figures 23-25. CxMe values for the three extractants at equilibrium are also shown for each sample vertically beneath the 'total' value. Clearly, the cxMe values are not simply related to the 'total' for each of the three elements. In a very broad sense there is some indication that a relationship exists, in that the general trend of any one cxMe plot is roughly the same as the trend of the 'total' plot. However, in detail the results show that for any range of values of 'total' metal there is almost a complete range of cxMe values.

For example, for the range 95-105 ppm 'total' copper, the cxCu value varies from 2 to 75 ppm. In order to investigate this phenomenon, a more detailed study of the samples themselves and the results obtained was made as described later in this section.

From Figure 25 it is clear that the cxZn values obtained using hydrochloric acid, EDTA/sodium chloride, or ammonium citrate extractants do not differ greatly. However, there is quite a wide variation for cxCu and cxPb for the three extractants over the whole concentration range (Figs 23, 24). Generally speaking, for all three metals, hydrochloric acid gives slightly higher extraction values than EDTA/sodium chloride and both give higher values than ammonium citrate. This does not mean that ammonium citrate is necessarily an inferior reagent for the cold extraction technique, because it is the sample to background ratio that is more important than the absolute metal content (Hawkes & Webb, 1962, p. 152). It is therefore unreasonable to be dogmatic in recommending one reagent in preference to another, for in certain circumstances both can be satisfactory. The choice of extractant should be made according to the type of sediment being used. For example, one would not use 0.1 M hydrochloric acid for cxMe values on a carbonate rich sediment (although M hydrochloric acid under the conditions 1 g sample to 40 ml extractant is quite good), nor could ammonium citrate be recommended for stream sediments very rich in iron for much of it will be lost in the form of iron citrate complexes. The economics of the situation might also be a factor to be considered and this is dealt with later in the 'Discussion' section.

The relationship between cxMe and 'total' metal content might be better understood if the mode of occurrence of the particular metals under investigation in the sediment were known. Some of the sediments used contained a large 'total' content of copper, lead, or zinc and it was thought likely that in some cases it would be possible to detect detrital minerals of these metals under the microscope. Some twenty-five selected samples from the batch were examined in both thin and polished section, and this investigation is described in Appendix B by I.R. Pontifex. No lead or zinc minerals, either primary or secondary, and no secondary copper minerals were seen in any of the samples. However, chalcopyrite was identified in some. Obviously a simple mineralogical examination is insufficient to fully complement the chemical work carried out on these samples, and at the moment one can only speculate as to the exact form of the metals in the sediments. Possibly a study of the reaction rates or the stability of complexes might resolve the problem, but so far little progress along these lines has been made.

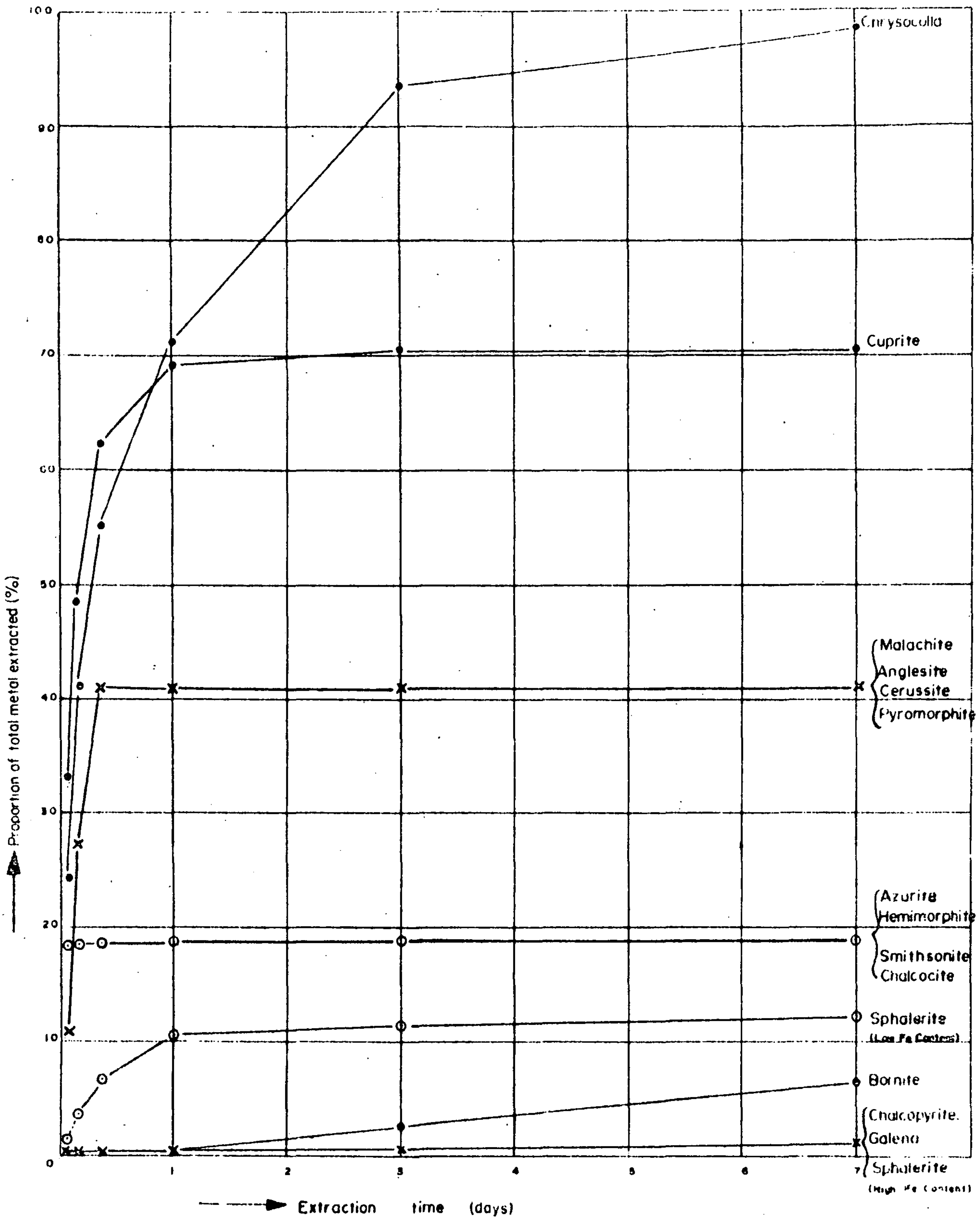
One factor that might influence the form which the metals take in the stream sediments, and hence the cxMe values, is the properties of the country rocks from which the sediments were derived. In the Herberton district three main rock types crop out and materials from these rocks make up the stream sediments. About 70 percent of the stream sediments are



To accompany Record 1970/11

Fig 19 Extraction of the major metal from the 80 – 150 B.S.S fraction of some minerals by 0·5 M ammonia citrate

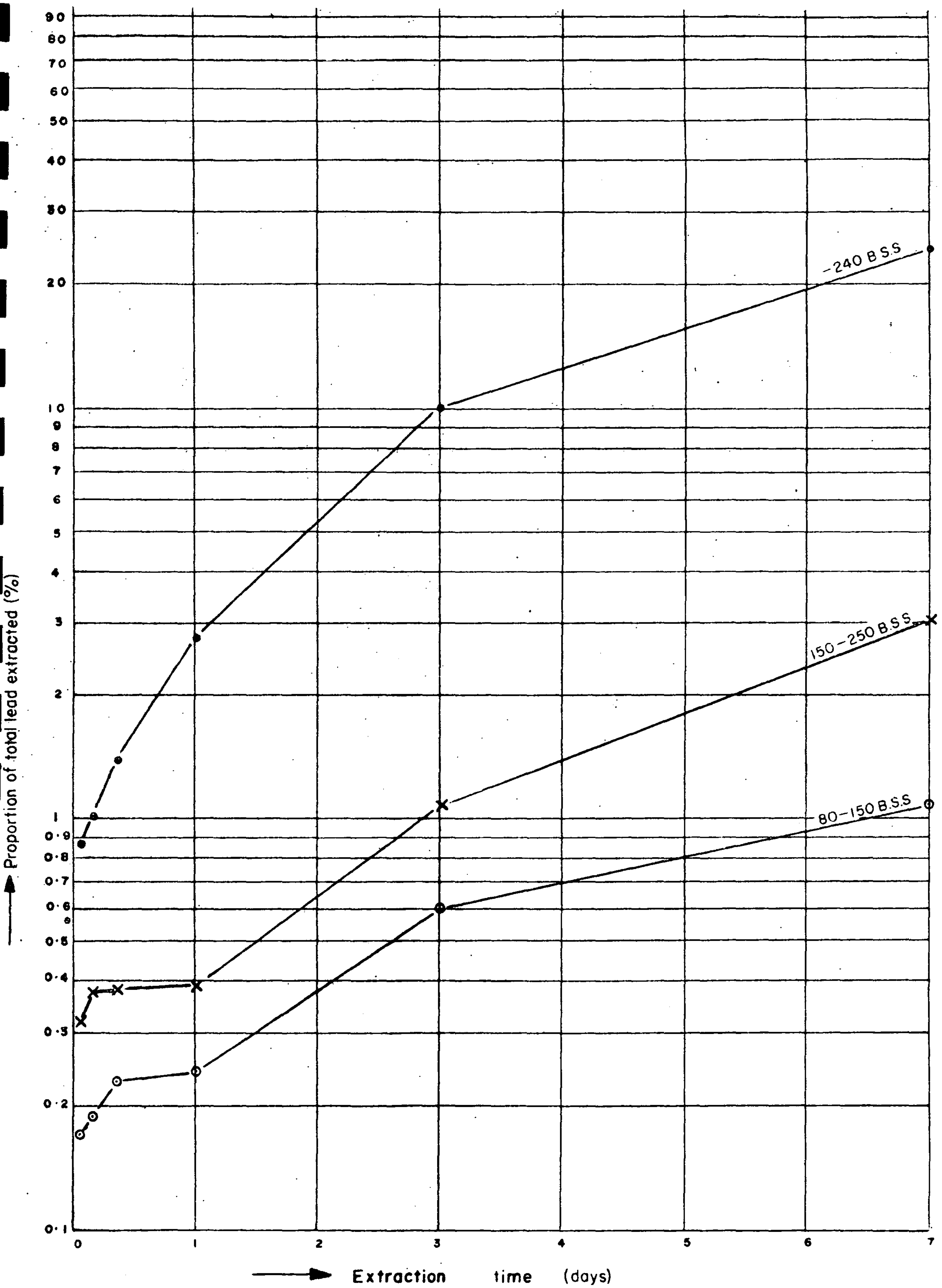
M(G)80



To accompany Record 1970/11

Fig 20 Extraction of major metal from the 80-150 B S S fraction of some minerals by 0 01M EDTA/0M sodium chloride

M(G)81 IM



To accompany Record 1970/11

M(G) 79

Fig 21 Extraction of lead from three size fractions of galena by 0·01M EDTA/0·1M sodium chloride

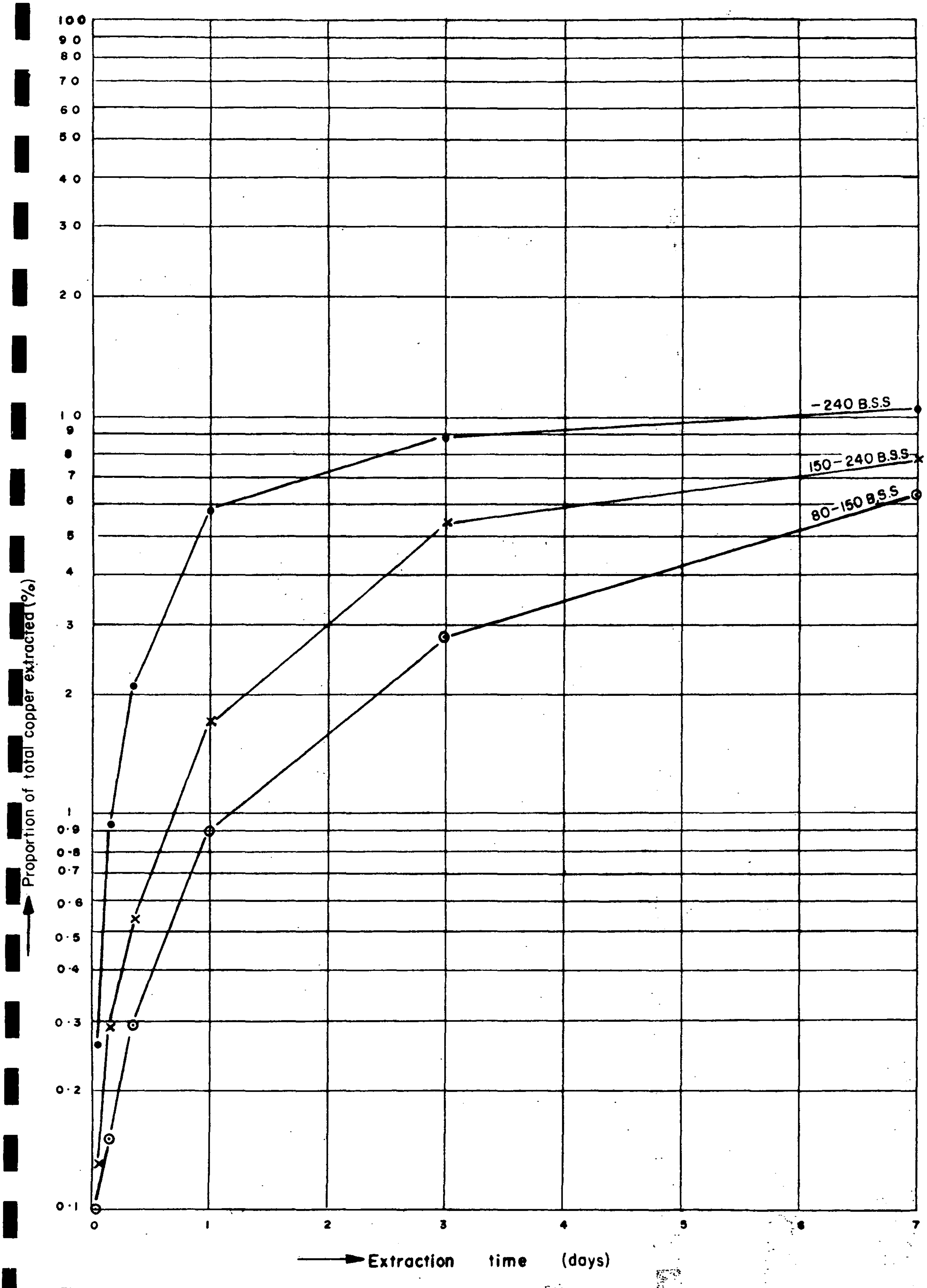


Fig. 22 Extraction of copper from three size fractions of bornite by 0·01M EDTA/0·1M sodium chloride

To accompany Record 1970/11

M(G) 77

To accompany Record 1970/11

M(G)22 EJ

Fig. 23 Partial and total copper analyses on 253 stream sediment samples from Herberton, Queensland, ground to pass 80 B.S.S. mesh.

To accompany Record 1970/11

M(G)23 EJ

Fig. 24. Partial and total lead analyses on 253 stream sediment samples from Herberton, Queensland, ground to pass 80 B.S.S. mesh.

To accompany Record 1970/11

M(G)24 EJ

Fig. 25. Partial and total zinc analyses on 253 stream sediment samples from Herberton, Queensland, ground to pass 80 B.S.S. mesh

TABLE 18. DISTRIBUTION OF COPPER VALUES IN STREAM SEDIMENT SAMPLES FROM HERBERTON, QUEENSLAND

	All Samples		Samples derived from sedimentary rocks		Samples derived from granites		Samples derived from acid porphyry		Samples derived from alluvium		Samples of uncertain derivation	
Range of copper values (ppm)	No in range	Percentage of total no of samples	No in range	Percentage of samples in range	No in range	Percentage of samples in range	No in range	Percentage of samples in range	No in range	Percentage of samples in range	No in range	Percentag of sample in range
2 - 6	25	10.0	8	32.0	5½	22.0	8½	34.0	1	4.0	2	8.0
2 - 9	54	21.7	25	46.3	9	16.7	17	31.5	1	1.8	2	3.7
2 - 12	98	39.4	50½	51.5	21½	21.9	23	23.5	1	1.0	2	2.0
2 - 16	129	51.8	74½	57.8	25½	19.8	26	20.2	1	0.8	2	1.6
2 - 22	161	64.7	92½	57.5	36	22.4	28½	17.7	2	1.2	2	1.2
2 - 30	189	75.9	111	58.7	40	21.2	32	16.9	2	1.1	4	2.1
2 - 79	221	88.8	132	59.7	48	21.7	34	15.4	2	0.9	5	2.3
2 - 1163	249	100.0	152	61.0	52½	21.1	37½	15.1	2	0.8	5	2.0

TABLE 19. DISTRIBUTION OF LEAD VALUES IN STREAM SEDIMENT SAMPLES FROM HERBERTON, QUEENSLAND

Range of copper values (ppm)	All Samples		Samples derived from sedimentary rocks		Samples derived from granites		Samples derived from acid porphyry		Samples derived from alluvium		Samples of uncertain derivation	
	No in range	Percentage of total no of samples	No in range	Percentage of samples in range	No in range	Percentage of samples in range	No in range	Percentage of samples in range	No in range	Percentage of samples in range	No in range	Percentag of sample in range
5 - 15	30	12.4	15	50.0	14½	48.3	½	1.7	0	0.0	0	0.0
5 - 22	64	26.3	29½	47.1	24½	38.3	8	11.7	2	3.1	0	0.0
5 - 30	94	38.7	47½	50.5	30	31.9	12½	13.3	2	2.1	2	2.1
5 - 43	127	52.3	71	54.9	35½	28.9	16½	13.0	2	1.6	2	1.6
5 - 52	158	65.0	94	59.5	39	24.7	20	12.7	2	1.3	3	1.9
5 - 75	186	76.5	110	59.1	45	24.2	25	13.4	2	1.1	4	2.2
5 - 150	215	88.5	129½	60.2	50	23.3	28½	13.3	2	0.9	5	2.3
5 - 1170	243	100.0	150	61.7	52½	21.6	33½	13.8	2	0.8	5	2.1

TABLE 20. DISTRIBUTION OF ZINC VALUES IN STREAM SEDIMENT SAMPLES FROM HERBERTON, QUEENSLAND

Range of copper values (ppm)	All Samples		Samples derived from sedimentary rocks		Samples derived from granites		Samples derived from acid porphyry		Samples derived from alluvium		Samples of uncertain derivation	
	No in range	Percentage of total no of samples	No in range	Percentage of samples in range	No in range	Percentage of samples in range	No in range	Percentage of samples in range	No in range	Percentage of samples in range	No in range	Percenta of sampl in range
6 - 24	32	12.9	15	46.9	11	34.4	5	15.6	1	3.1	0	0.0
6 - 32	68	27.4	29½	43.4	28	41.2	9½	14.0	1	1.5	0	0.0
6 - 43	98	39.5	44½	45.4	35½	36.2	16	16.3	1	1.0	1	1.0
6 - 57	126	50.8	63	50.0	39½	31.3	19½	15.5	2	1.6	2	1.6
6 - 76	157	63.3	83½	53.2	47	29.9	22½	14.3	2	1.3	2	1.3
6 - 105	186	75.0	104	55.9	49	26.3	27	14.5	2	1.1	4	2.2
6 - 154	216	87.1	127½	59.0	52½	24.3	30	13.9	2	0.9	4	1.9
6 - 622	248	100.0	151½	61.1	53	21.4	36½	14.7	2	0.8	5	2.0

derived from sedimentary rocks, about 17 percent from granite areas, and the remainder from acid volcanics. One cannot readily distinguish by mineralogical examination between the stream sediments derived from sedimentary rocks and those derived from granites in this district, whereas the stream sediments derived from acid volcanics are easily distinguished. In the following study, copper, lead, and zinc are treated separately, and no attempt is made to correlate with one another the total or extractable values for copper, lead, or zinc.

Table 18 shows the number of samples from each rock type in various ranges based on the aqua regia 'total' copper content. The high copper values tend to be associated more with stream sediments derived from sedimentary rocks than with stream sediments derived from acid volcanics, but there is no clear pattern established for stream sediments derived from granites.

The results obtained for lead and zinc have been treated similarly to those for copper. The results and computations are given in Tables 19 and 20. The high lead and zinc values tend to be associated more with sediments derived from sedimentary rocks and less with those from granites. There is no tendency for those from acid volcanics to become enriched in lead and zinc.

Most of the peak cxMe values shown in Figures 23-25 were obtained on stream sediments that were collected from points only a few hundred yards down-stream from known mines or adits. Some, however, were obtained on stream sediments derived from areas not known to be mineralized, and these were higher in some cases than those from creeks draining the mining area. These areas warrant further investigation, but this pursuit is beyond the scope of the present program.

DISCUSSION

The main cost in a geochemical exploration survey is sampling. Excluding the cost of vehicle etc, labour costs for collection alone in rough country amounts to about $1.50 per stream sediment sample, if about 10 samples are collected per man-day. The cost of chemicals required for the analysis of 50 samples by the various methods are shown in Table 21. By far the cheapest extractant is hydrochloric acid.

TABLE 21. ESTIMATED COST OF CHEMICALS OR ELECTRODES FOR THE ANALYSIS OF 50 STREAM SEDIMENT SAMPLES

Method of Analysis	Cost per 50 samples ($)
0.1 M hydrochloric acid extraction	0.02
0.01 M EDTA/0.1 M sodium chloride extraction	0.12
0.5 M ammonium citrate extraction	0.18
Optical spectrograph	2.00 (electrodes)
Aqua regia digestion	0.09

In addition to the cost of chemicals, electrodes etc., there is also the analyst's time, and the cost of instrument time such as optical spectrograph or atomic absorption spectrophotometer; these amounts to a minimum of $1.00 per sample. Thus, each stream sediment sample costs at least $2.50 to collect and analyse, and only a very small part of this is for chemicals or electrodes. The cost per element by spectrographic method is minimized because several elements can be determined with each analysis. Probably a fairer way of comparing costs is on the basis of cost per element, although this can give rise to false costing by including elements which are only rarely, if ever, present. It appears that the difference in the cost per analysis by the various methods is insufficient to influence the choice of analytical method, and that choice should depend on suitability and convenience of the method for the solution of a particular problem. When analyses are required in the field, cold extractions followed by a colorimetric method of analysis are convenient. If, however, it is possible to get the samples back to a laboratory for analysis, it appears that an aqua regia attack is preferable. Provided that the reasons for wanting cxMe values are sound, for example, where absolute total metal values are not required, then the value obtained by aqua regia extraction should be satisfactory, though it must be realized that even with this procedure the breakdown of some silicate minerals may occur.

Considering the results as a whole, however, it appears that geochemical anomalies will be detected by whatever method is used, provided that reasonable care is taken with the analyses. Anomalous areas are not often delineated on the basis of one sample. The general tendency, as we have seen, is for the extractable metal value to follow the 'total' metal value, and therefore the method to be used for the batch of samples concerned might as well be the convenient one.

CONCLUSIONS

The main conclusions to be drawn from this investigation may be summarized as follows:

(1) The cxMe value obtained depends mainly on the type of extractant used, and only slightly on the concentration of the extractant.

(2) The particle size of a stream sediment affects the cxMe value obtained. Generally speaking, the smaller the particle size, the greater the cxMe value obtained.

(3) Complex formation and low pH are important factors in the extraction of copper and zinc.

(4) Equilibrium cxMe values are sometimes obtained only after leaching for periods of up to 6 or 7 days. However, for the purposes of geochemical prospecting, short leaching times might be suitable even though equilibrium is not established.

(5) Drying of a stream sediment sample lowers the rate of extraction of metals from the sample, and increases the time necessary to establish equilibrium to twenty and more days in some cases. The higher the temperature of drying, the slower the subsequent extraction. However indications are that the final equilibrium extraction value for copper and zinc might be independent of drying out, provided that sufficient time is given for extraction.

(6) Both primary and secondary minerals contribute to the cxMe values, but secondary minerals make by far the greater contribution. The sulphide minerals are only slowly attacked by weak extractants, but it is interesting to note that they are not inert as is so often believed. Minerals such as azurite and malachite are readily attacked.

(7) Generalizing from the results obtained on the 253 stream sediment samples from the Herberton area, individual cxMe values are not simply related to the 'total' metal values, whatever the extractant.

(8) The mode of occurrence of the metal in the sediment affects the cxMe value much more than the type of gangue material.

RECOMMENDATIONS

The results of these studies suggest that cxMe values are no better, and in some cases worse, than 'total' metal values in the search for hidden orebodies. Therefore, for the analysis of stream sediments in geochemical prospecting, it is suggested that a carefully obtained aqua regia determination is preferable to a cxMe value or a spectrographic 'total' metal value. However, on occasions, cold extraction techniques may be more convenient than an acid digestion.

In many parts of Australia there is no choice between wet and dry sampling and judging from the results reported in earlier sections, it matters little whether the stream sediments are sampled wet or dry. For convenience of handling both in the field and in the laboratory, it is preferable to submit dry samples even if they are sampled wet.

The generally accepted particle size range for stream sediment sampling is less than 80 B.S.S. mesh. Even though smaller particles often give higher 'total' metal content or higher cxMe values, the sieving time required to get enough of these samples for analysis is unnecessarily long, and the higher values do not provide any more useful information in the search for anomalous areas. Therefore, the continuation of the 80 mesh sampling technique is recommended.

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APPENDIX A

MINERALOGICAL EXAMINATION OF GEOCHEMICAL STREAM SEDIMENT SAMPLES FROM SAPPHIRE CREEK, PAPUA AND PADDYS RIVER A.C.T.

by

I.R. Pontifex

The samples were submitted by J.R. Beevers; they are stream sediments of the size fraction -80 + 120 mesh which have been chemically analysed as part of a trace element distribution study.

Method of Analysis Each sample was separated into a light and heavy fraction in bromoform. Magnetite was removed from the heavy fraction with a hand magnet. The components of each fraction were examined under a binocular microscope and in R.I. liquids under a petrological microscope and this enabled the percent of minerals in each fraction to be estimated on a semi-quantitative basis.

1. Stream sediment sample from Sapphire Creek, 29 km east of Port Moresby. The drainage pattern of this stream covers clastic sediments of the Port Moresby Beds, gabbro and agglomerate. Two old copper mines also occur in the area drained up-stream from this sample.

a. Light fraction.

The approximate proportions of mineral grains in the light fraction are as follows:-

iron hydroxide (limonite)	30%
fragments of volcanic matrix	20%
plagioclase feldspar	20%
quartz	15%
ferromagnesian minerals	10%
orthoclase feldspar	5%

Comments

Iron hydroxide These grains consist dominantly of limonite, they are irregular in shape and commonly porous. This mineral appears to have formed in two ways:

a. by replacing iron-rich minerals by chemical alteration,
b. by thoroughly impregnating the alteration products of partly or completely altered minerals such as feldspars and amphiboles.

Fragments of volcanic matrix These are present as fairly rounded grains which consist of cryptocrystalline aggregates of quartz and feldspar. A positive identification of these grains is difficult since they are generally densely clouded and impregnated with iron. This cloudiness appears to be the result of alteration of the feldspars and disseminated iron-oxides in the matrix.

It is suggested that these grains are derived from the volcanic agglomerate which crops out on the plateau above Sapphire Creek.

Plagioclase Feldspar The exact composition of these grains is difficult to determine; refractive index comparisons suggest that most of them are a basic variety, however, several grains of albite and oligoclase were identified. The grains are angular and commonly show well defined cleavage faces, generally they are moderately altered and stained with iron.

Quartz The quartz grains are angular, some contain dust and fine needle-like inclusions of rutile and the surfaces of some are pitted.

Ferromagnesian minerals. Most of these appear to be partly altered amphiboles although minor amounts of chlorite are present.

This study suggests that most of the citrate soluble metal ions in this fraction will be associated with the iron-hydroxide grains and the altered fragments of volcanic matrix.

b. Non-magnetic heavy fraction.

The approximate proportions of minerals in this fraction are as follows:

iron hydroxide	30%
amphibole, mainly hornblende, some actinolite	25%
hematite	10%
epidote	10%
pyrite	5%
rutile	5%
opaque grains (?ilmenite)	5%

feldspar	5%
pseudomorphs of limonite after pyrite	3%
chalcopyrite) malachite) azurite)	minor-accessory amount

Comments

Limonite Has the same form as the limonite described in the light fraction.

Amphibole The amphibole grains commonly occur as freshly broken euhedral grains. The most abundant variety is hornblende; this generally contains inclusions of iron-oxide and is slightly altered. Hematite occurs as irregular broken grains, some of these appear to be finely micaceous.

Pyrite grains are angular and generally freshly broken; some have retained part of their original euhedral form.

Feldspar The identification of the type of feldspar is not possible since they are densely clouded with alteration products.

In this fraction it seems that absorbed trace metals would be associated with the limonite and to a lesser extent with alteration products of the amphiboles. The presence of accessory amounts of chalcopyrite and copper carbonates would cause high copper values in this fraction, relative to the light fraction or the magnetite.

c. Magnetite fraction.

This consists essentially of magnetite some grains of which are slightly oxidised to hematite. The separation method of magnetite has caused a contamination of this fraction with about 15 percent of non-magnetic heavy minerals.

2. Stream sediment sample from Paddys River, approximately 22 km west of Canberra. This stream drains porphyry and a skarn zone. Two collapsed adits with accompanying dumps from small copper, lead, and zinc mines occur about 200 m up slope from the sample point.

a. Light fraction

The approximate proportions of mineral grains in the light fraction are as follows:

chlorite and subordinate biotite	40%
quartz	20%
feldspar	20%
muscovite and sericite	15%
limonite stained grains	5%

All the components except the quartz are generally clouded with alteration products. Some of the chlorite appears to be altered to talc. The muscovite and feldspar are moderately to extensively altered to various clay minerals.

b. Heavy fraction

The approximate proportions of mineral grains in the heavy fraction are as follows:

epidote	25%
amphibole	25%
zircon	20%
limonite stained and impregnated grains	10%
garnet	10%
ilmenite-leucoxene	5%
pyrite	3%
hematite	3%
pseudomorphs of limonite after pyrite	2%

The amphibole, garnet, limonite and ilmenite grains are difficult to identify since most of them are coated with fine alteration products, therefore an accurate estimation of their abundance is not possible.

c. Magnetite fraction

This consists entirely of magnetite grains almost all of which are partly oxidised to hematite.

APPENDIX B

A MINERALOGICAL EXAMINATION OF GEOCHEMICAL STREAM SEDIMENT SAMPLES FROM HERBERTON AREA; NORTH QLD

by

I.R. Pontifex

J.R. Beevers submitted 25 stream sediment samples for mineralogical examination which he analysed by various methods for their total and cold extractable content of Cu, Pb, Zn, and Sn. The aim of this investigation was to determine the nature and abundance of the mineral components in each sample so that a comparison can be made between variations of these and variations of the trace element content.

A thin-section and a polished-section of each sample were examined and the amount of each component was estimated by comparison with charts showing different percent concentrations.

The results are tabulated below and this is followed by comments on the nature of each component. All figures are given as percent; -1 means that several grains of a mineral were recognized in the section but these would generally form of the order of 0.01 percent.

Component / Sample	080022	080504	080512	080533	080540	080581	080589	080598	080629	080635	080642	080645	080651	080653
quartz grains	30	75	60	60	40	70	45	50	45	60	45	75	70	10
frags. of sed. rock	25	15	30	30	40				40	30	45	15	20	
frags. of vol. rock	15					10	10							80
feldspar (plag.)	5	1-3	3-5	3-5			3-5	20	5	5	5	8	2	
feldspar (K.)	3-5						45	20					2	1-3
amphibole (chloritized)	3-5			3-5		5			5	-1		3-5		
micaceous minerals	5				1	5	3-5	5					3-5	5
zircon	1	-1		-1								-1		2
blue tourmaline								2					-1	
unidentified detritus					10									
cassiterite	-1				-1	-1	-1		-1	-1				
limonite	2	3-5	1		5	2				1	1	2		2
iron oxide grains	3	3	2	2	5	2	1	3			1	2		2
pyrite	2		-1	1	2	1	-1	2	3	2	2	2		
chalcopyrite	-1			-1					-1		-1	-1		

Component / Sample	080655	080662	080672	081007	081012	081030	081038	081040	081057	081061	081066
quartz grains	10	3-5	70	65	70	60	50	55	50	30	60
frags. of sed. rock			15	25	10	15	5	15	30	55	15
frags. of volc. rock	80	85					10	10			
feldspar (plag.)			1	2		7	2	5	5		
feldspar (K)	1-3			2	1-3	3	3	2		5	
amphibole (chloritized)						3-5	10		5		5
micaceous minerals	5	3-5	10	3-5		10		10	10	5	5
zircon	2	3	2								-1
blue tourmaline							3-5				
unidentified detritus											15
cassiterite	-1	2	2				1				
limonite	2				15	2	15	3-5	3-5	3	3
iron oxide grains	2	2		1	5	1	3	2		3	2
pyrite			-1				2	1	2		
chalcopyrite		-1									

Comments

Quartz grains. The majority of these are free although in some samples, particularly in those containing volcanic rock fragments, they form composite grains with fine-grained sericitic matrix. In sample 0800662 the quartz grains are embayed which indicates that they are phenocrysts, derived from a porphyritic rock. In samples 081012, 081040, 081057, the quartz grains have a fine coating of iron-stained alteration products.

Fragments of sedimentary rock. These generally appear to be derived from shale, siltstone and fine-grained greywacke. Typically they consist of a fine-grained aggregate of quartz and minor amounts of sericite and chlorite. The fragments also contain accessory fine opaque grains and commonly they are stained with iron-oxides.

Fragments of volcanic rock. These consist of a fine-grained micro-mosaic of quartz, which generally contains subordinate amounts of feldspar, sericite, chlorite, and dusty opaque grains. The matrix is generally clouded by iron-stained alterations products of the matrix. These components appear to be acid volcanic detritus and the fragments are probably derived from tuffs.

These fragments are similar to those of fine-grained greywacke and it is not possible to positively identify all of them, however their crystalline form and inclusions of feldspar and quartz phenocrysts do indicate that they have an acid igneous origin.

Feldspar grains. These occur both free and as composite grains with adhering fine-grained matrix. Most of them appear to be unaltered although some, more commonly K feldspar, show some alteration to clays. The plagioclase grains are within the albite-oligoclase-andesine range of composition. The K feldspar is predominantly microcline.

Amphibole. This occurs most commonly as hornblende which is partly altered to chlorite.

Micaceous minerals. Muscovite and chlorite flakes are generally associated with samples derived from sedimentary rocks but they also occur, together with biotite, in samples which contain fragments of acid volcanic rocks. The biotite and chlorite are commonly stained by, and chlorite is partly altered to, iron-hydroxides.

Zircon and blue tourmaline occur as free grains.

Unidentified detritus. Most samples contain between 1 percent and 3 percent of fine dust-like material which is impossible to identify. In samples 080540 and 081066 however this material makes up 10 percent and 15 percent of the sample respectively. Most of this material in both sections appears to be of organic origin.

Cassiterite occurs as free grains.

Limonite generally stains alteration products (clays etc.) in the matrix of the rock fragments; in most sections however (notably 081012) it also occurs in free grains. The limonite is probably derived by the alteration of previously existing grains of iron-oxides and possibly sulphides.

Iron-oxides consist of various mixtures of hematite, hydrated iron-oxides and subordinate magnetite. Free grains of the same size as the silicate grains are common; in addition, irregular patches are also included in the silicate grains and rock fragments.

Pyrite rarely occurs as free grains. It was most commonly observed as fine grains (0.07 mm.) and skeletal masses within silicate grains.

Chalcopyrite grains also rarely occur free, but the size of some that were observed are as follows:

sample	size in mm.
080022	0.005
080533	0.003
080629	0.01 and 0.003
080645	0.05
080662	0.02 and 0.005