

GROUND WATER ANALYSIS FOR SELECTED IONS OF
TYPICAL WELLS IN THE EMPORIA, KANSAS VICINITY

A Thesis

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CHAPTER I

INTRODUCTION

Ground water in the Emporia vicinity was analyzed to determine the mineral content found in the water. The analysis was carried out to determine the acidity, the ionic concentration by conductance, the water temperature, and the calcium ion, magnesium ion, bicarbonate ion, chloride ion, and sulfate ion concentrations. These ions are aqueous constituents of ground water found in this area.

Emphasis was placed upon the development of the method for determination of the sulfate ion, because there is no accepted accurate method for its determination.

The water used in the analysis was obtained by periodic sampling of selected wells outside of the Emporia city limits. The samplings were made from untreated taps which were used for domestic purposes or for livestock watering. The tests for water temperature and acidity were made at the sampling location using a thermometer and a portable pH meter. The remainder of the analysis was done in the Kansas State Teachers College chemistry laboratories.

Ground water is the water below the surface of the land that supplies water to wells and springs. The origin of the water which becomes ground water is primarily precipitation or seepage from streams. The amount of mineral content found in such water is dependent on the source of the water and the medium through which it is flowing. The water retains any soluble ion which it has dissolved or has been dumped into it.

Emporia is located between the Cottonwood and Neosho Rivers. The areal geology points out that Emporia is located almost entirely on terrace gravel and alluvium deposited by the two rivers.¹ A preliminary investigation was initiated to determine if the ground water found in cross-sections of the terrain on the upriver and downriver sides would yield any decrease or increase of the major common mineral content. The data obtained will determine the presence of permanent and temporary hardness, and indicate varying ionic concentrations at each location sampled over a two month period. This investigation represents the only recent ground water analysis data for this area. The methods for analysis of the ions determined in this study are outlined to provide easy, rapid, and relatively accurate procedures for primary ground water analysis.

CHAPTER II

EXPERIMENTAL PREPARATION AND ANALYSIS

There are many different opinions of what method to use in the analysis of water. Each method is the result of studies made on different types of water found in various areas. All of the methods have some importance in studying the type of waters which the methods were developed to analyze. The various methods lack specific ion accuracy because there are ion similarities. All of the methods used in this study are outlined in the book Standard Methods for the Examination of Water, Sewage, and Industrial Wastes. This book is the source of the procedures presently followed by the Kansas Water and Sewage Laboratory. Some of the analytical procedures employed in this investigation are revisions of these standard procedures.

As an insight to the probable limits of the concentration of the ions to be determined, a literature search was made to find any available material. The literature available on ground water in Lyon County is very limited. The only published information about Lyon County ground water which is known to the University of Kansas Publication Director, Mr. Diaz of the U. S. Geological Survey, and Mr. Stoltenberg of the Water and Sewage Laboratory of the Kansas State Board of Health, is but a single publication, "Geology, Mineral Resources, and Ground Water Resources of Lyon County, Kansas" Part 3 by Howard G. O'Connor (1953). The analysis in this study was only a single sampling of some thirty-three wells in the entire county. The laboratory work was done by the state laboratories. In the study, only two of the wells sampled were located in the vicinity of the well sites in this study.

Preparation of Solutions

The solutions for these analyses were prepared from reagent grade chemicals. The burettes used in the titration analyses were three-way Teflon stopcock, class A, Kimax microburettes and straight Teflon stopcock, class A, Kimax microburettes.

Conductance Analysis

The only prepared solution used in this analysis is a standard 0.100 N KCl solution which was prepared by adding 0.7456 grams of Baker Reagent Grade Potassium Chloride to make one liter of solution.

pH Analysis

The standard base used in this analysis was prepared from Mallinckrodt Sodium Hydroxide. Due to the fact that sodium hydroxide solid absorbs water rapidly, the solution was prepared by weighing approximately 8 grams of the solid and pouring that into a two liter volumetric flask. Deionized water was then added to the mark. Small samples of dried Mallinckrodt Primary Standard Potassium Biphthalate were weighed and solvated with 50 ml deionized water and then titrated with the prepared sodium hydroxide to a phenolphthalein endpoint.

The hydrochloric acid used in the analysis was prepared by pipetting 16.6 ml of concentrated Mallinckrodt Hydrochloric Acid into a liter of water and then diluting to two liters. To standardize the acid, a 5.00 ml aliquot was taken and titrated with standard NaOH to a phenolphthalein endpoint.

The indicator, phenolphthalein was prepared by dissolving 1 g solid phenolphthalein in 100 ml 60% ethyl alcohol.

The indicator, bromocresol green, was prepared by dissolving 0.10 g solid bromocresol green in 100 ml 20% ethyl alcohol.

Chloride Analysis

The reagent for this analysis was 0.10 N silver nitrate. It was prepared from dried Reagent Grade Silver Nitrate. A liter of solution was prepared from 16.991 grams of the dried solid. The solution was standardized using small dissolved samples of dried Baker & Adamson Reagent Grade Sodium Chloride.

The indicator used in the analysis is the absorption indicator, dichlorofluorescein. It was prepared by dissolving 0.10 g of dichlorofluorescein in 100 ml 70% ethyl alcohol.

Calcium-Magnesium Analysis

The reagents used in sample preparation were concentrated nitric acid, methyl red indicator and 2.5 M sodium hydroxide.

The nitric acid was Reagent Grade Baker & Adamson stock.

The 2.5 M sodium hydroxide was prepared by dissolving 10.0 grams of sodium hydroxide pellets in water to a volume of 100 ml.

The methyl red indicator was prepared by dissolving .1 g methyl red indicator into 250 ml 60% ethyl alcohol.

The titration reagents were composed of 0.1 disodium ethylenediaminetetraacetic acid (Na_2EDTA), a pH 10 buffer, .1 M MgSO_4 and Eriochrome Black T indicator.

The Na_2EDTA was prepared by weighing 37.255 grams of the solid into a liter volumetric flask and diluting to the mark.

The magnesium sulfate was prepared by weighing 11.960 grams of dried Mallinckrodt Analytical Reagent Magnesium Sulfate into a liter

volumetric flask and diluting to the mark. This was then standardized using the Na_2EDTA solution.

The pH 10 buffer was prepared by diluting 570. ml of Mallinckrodt Analytical Reagent Grade Ammonium Hydroxide (sp. gr. 0.90) and 70. g of Mallinckrodt Analytical Reagent Grade Ammonium Chloride to a liter with deionized water.

The Eriochrome Black T indicator was prepared by dissolving 0.10 grams of Matheson, Coleman & Bell Eriochrome Black T in 25 ml of Mallinckrodt Analytical Reagent Grade Methanol.

Sulfate Analysis

The solutions necessary for the sulfate analysis were standard sodium sulfate, 1 M barium chloride and the conditioner.

The standard sulfate solution was prepared from Matheson, Coleman & Bell Reagent Grade Sodium Sulfate. The solution was made to a concentration of 113 ppm by adding 0.1673 grams of dried Na_2SO_4 to a liter volumetric flask and diluting with deionized water.

The BaCl_2 solution was prepared by adding 66.0 grams of Mallinckrodt Analytical Reagent Grade Barium Chloride, dihydrate, into a 250 ml volumetric flask and diluting with deionized water.

The conditioner was prepared by first dissolving 25 ml Mallinckrodt Glycerine in 50 ml Mallinckrodt N. F. Isopropyl Alcohol. This was followed by addition of 150 ml deionized water and 38 grams of Baker & Adamson Reagent Grade Sodium Chloride. The final additive was 15 ml of Mallinckrodt Reagent Grade Hydrochloric Acid.

Procedure

Sampling Preparation

After setting general sampling locations, the next aspect of the project entailed the cleaning of an appropriate number of two liter glass bottles. Each bottle was first washed with soap solution and rinsed in tap water. This was followed by adding a coating of nitric acid and sodium dichromate cleaning solution. These were rinsed in tap water and then about fifty milliliters of one molar disodium ethylenediamine-tetraacetic acid was rinsed through each bottle to remove any complexable metals present. Finally, the bottles were rinsed several times with deionized water and allowed to dry overnight.

Sampling Procedure

All of the samples were taken from an untreated faucet at or near the well proper. At the time of sampling, the wells were either being used or if not several gallons of water was discharged before the sample bottle was filled. The thermometer was rinsed and a test tube of water was taken for pH determination after the bottle filled.

Determination of Water Temperature

~~After filling the sample bottle, the rinsed Fisher Scientific Partial Immersion Thermometer was immersed on location.~~

Determination of pH

At the sampling site, the Orion Research Ionalyzer Specific Ion Meter Model 404 was adjusted using the standard buffer. The Sargent Combination Calomel-Glass Electrode was then inserted into the test tube and the pH read directly from the meter.

The remainder of the water analyses was carried out in the laboratory.

Determination of Conductance

Conductivity measures the ability of a material to conduct an electrical current. The conductivity of water is proportional to the concentration of the cations and anions present and the temperature of the sample. Conductivity values were obtained by first calculating a cell constant using a solution of known conductivity. The resistance of this solution was measured and the cell constant calculated from the following relationship:

$$\text{cell constant} = \text{conductivity} \times \text{resistance}$$

A standard solution of 0.10 molar potassium chloride was used as the known. It had a defined conductivity of 1412 micromhos. The experimental resistance was determined to be 725 ohms. The calculated cell constant was 1.24.

The instrument used in the analyses was an Industrial Instrument Type RC Conductivity Bridge. The conductivity cell contained a pair of platinum discs coated with platinum black. The discs were 1.2 cm in diameter and 3.0 cm apart.

The determination was made by pouring a 150 ml aliquot of sample in a 180 ml tall form beaker. The cell was rinsed several times with deionized water and air dried. The cell was then submerged in the sample and the reading was taken as experimental conductance. The conductivity of the water samples is equal to the cell constant C times the experimental conductance Cx.

$$\text{Conductivity} = C \times Cx$$

An estimate of the milliequivalent concentration of anions or cations can be made by multiplying the conductance by 0.01.^{1,7}

Determination of Carbonate-Bicarbonate

Since much of the rock in the area is limestone, it appears logical that there would be an appreciable amount of carbonate and bicarbonate found in the water. The pH of the water samples was found to range from 6.6 to 7.3. The titration curve of sodium carbonate with hydrochloric acid (Figure 1),³ indicates that carbonate ion is essentially non-existent at these pH values.

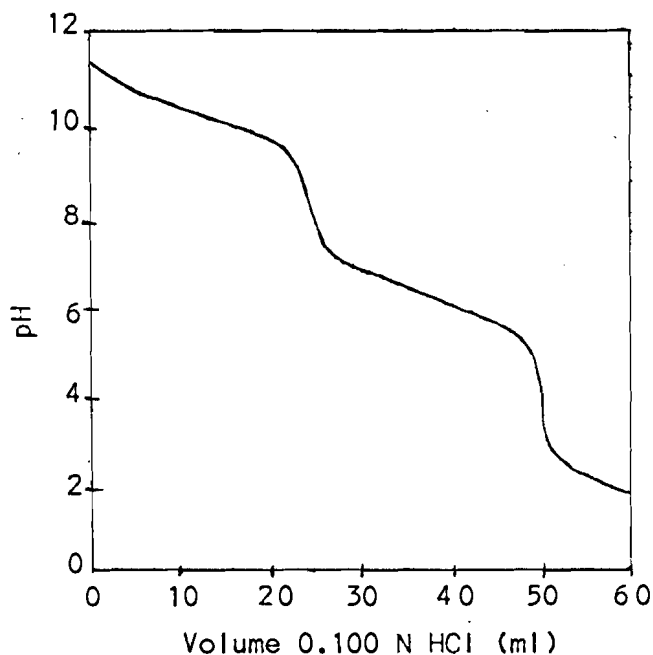


FIGURE 1

CURVE FOR THE TITRATION OF 2.5 ML 0.100 F Na_2CO_3 WITH 0.100 N HCL

Bicarbonate that would be present at the observed pH was determined by the titration of a 50 ml aliquot of the water sample with 0.100 N HCl. The acid was added to a bromocresol green endpoint. The solution was then boiled to remove dissolved carbon dioxide and then the titration was completed.³

Determination of Chloride

Two possible sources of chloride ion are sodium chloride deposits and calcium chloride from underground deposits or as a salt for melting ice and snow. There are two generally used methods for chloride determination. They consist of the gravimetric and volumetric precipitation techniques. Both employ silver ion as precipitation agent and in this investigation it appeared reasonable to use the faster volumetric method. There are several variations of the volumetric technique. The endpoint may be determined with indicators, by conductivity changes or by potential changes with suitable indicator electrodes. The use of this method neglected the interference from bromide and iodide that may have been present in small quantities. Previous work indicates that these ions are found in negligible amounts.¹

The analysis was of a 50 ml aliquot of sample. To the sample was added 3 drops of dichlorofluorescein indicator. The silver nitrate solution was added with vigorous stirring. About 1 percent before the endpoint, flocculation occurred. The titration continued until the precipitate obtained a light pink color.⁴

The concentration range of this technique was reported to be 0.025 N to 0.005 N,³ but from the subsequent data it appears that the procedure was useable down to about 0.002 N.³

TABLE 1

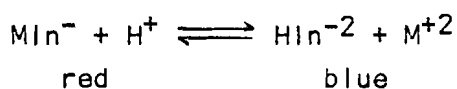
STANDARDIZATION OF AgNO_3 SOLUTION USING LOW CONCENTRATION CHLORIDE

Sample of NaCl in 50 ml H_2O	Normality of NaCl	Volume of AgNO_3	Normality of AgNO_3
0.02056g	0.0070	3.45 ml	0.0994 N
0.00945g	0.0032	1.62 ml	0.0998 N
0.00592g	0.0020	1.00 ml	0.1010 N

This data does not however go to the lowest level in which it is felt that the method will detect. At the lowest concentration titrated for standardization of the silver nitrate, the endpoint was well defined. These values are relatively accurate considering the standardization using higher concentrations yielded a value of 0.1008 N for the standard silver nitrate solution.

Determination of Ca^{+2} and Mg^{+2}

The most commonly used technique for the determination of calcium and magnesium is that of compleximetric titration with ethylenediaminetetraacetic acid. A compleximetric titration of calcium and magnesium can be completed in about five minutes. The disadvantage of the method is that many other metal ions also complex and interfere with the analysis. Iron would probably be the only significant interference in the data to follow. Ca and Mg complex most readily at a pH of over 10, for this reason it is necessary to maintain this pH continually. This is provided for by the ammonia buffer. This technique was developed for determination of hard water. The 50 ml aliquot sample is acidified with one or two drops of concentrated nitric acid and boiled. This is done to prevent the precipitation of calcium carbonate.⁷ The cool solution is then neutralized with NaOH to a methyl red endpoint. The combined calcium and magnesium concentration is determined by taking this sample and adding 2 ml of the ammonia buffer and 3 drops of Eriochrome Black T indicator and titrating with disodium ethylenediaminetetraacetic acid (Na_2EDTA). The color change is from red to blue for this titration. This is because reaction of the metal with the indicator.



M is the metal and In^{-3} is the indicator. With the Na_2EDTA competing with the indicator for the metal, the color change appears only at the point where essentially all of the metal ion has been complexed with the Na_2EDTA .³

The calcium determination was made by back titration of the above solution. The solution is taken and back titrated to a red color with standard MgSO_4 .³ It should be noted that if the magnesium present is small in relation to the calcium present, the method for magnesium is somewhat uncertain.⁷

Determination of Sulfate

At present, there are few rapid methods for determination of sulfate. There are even fewer techniques which provide reproduceable, accurate data. For this reason several different methods for determination were attempted unsuccessfully. They ranged from the precipitation by barium chloride with back titration with EDTA to the direct titration with barium chloride using the indicator tetrahydroxyquinone (THQ). These techniques entail many step procedures or misleading endpoints. It was finally decided to do the determination by turbidimetry. This technique is a fast, direct method for the sulfate determination. The sulfate ion is precipitated with barium ion in acid solution in such a manner as to form barium sulfate crystals of uniform size. Light is then passed through the solution and the amount of light blocked off by the precipitate is proportional to the concentration of the sulfate ion present in the solution. For the particle size to be uniform, there must be uniform mixing of the solution and the rate of addition of barium chloride must remain constant. It is known that an acid solution will allow relatively uniform particles growth, but the problem was to find a suitable solution that when added would also keep the particles in suspension to stabilize

readings. The solution used was a mixture of hydrochloric acid, sodium chloride, isopropyl alcohol, glycerine, and water. It was called the conditioner.²

The method for making the calibration curve followed a standard procedure. A 50 ml aliquot of sample was to be used for the unknown samples. To make the curve, 2 ml, 4 ml, 6 ml, 8 ml, 10 ml, 12 ml, and 14 ml of standard sulfate solution was mixed with the required remainder of deionized water to obtain a 50 ml aliquot. At the time of use, the solution was mixed with 10 ml of the conditioner and set on the constant rate magnetic stirrer. After agitating for several seconds, two ml of 1 M barium chloride was added rapidly via a 50 ml burette. At the instant of addition, the timer was started. The solution was stirred for one minute and then set aside to allow for particle growth. Four minutes after stirring, the solution was introduced into a Coleman 14 cuvette and inserted into the sample side of the cuvette carriage. The blank compartment of the carriage contained a cuvette containing a blank solution made of 50.0 ml deionized water, 10.0 ml conditioner, and 2.0 ml of 1 M barium chloride. The sample carriage was then inserted into the sample compartment of the Coleman Model 14 Universal Spectrophotometer and the instrument zeroed with the blank solution at a wavelength of 425 millimicrons. The readings of the sample were taken 5 minutes, 6 minutes, and 7 minutes after stirring ceased. After each reading the instrument's 100% transmittance was reset. A great deal of time was taken to find a procedure which would give three consistent galvanometer readings. Several problems were overcome by this work. For a long period of time, it was unknown why the galvanometer fluctuated continually. This was found to

be due to the evaporation of the alcohol in the blank over a long period of time. This was corrected by shaping a rubber stopper to tightly seal the blank cuvette. This stabilized the galvanometer effectively. Another problem found, was that after a short time the barium chloride at such concentrations began to cloud when exposed to air even in the stoppered bottle. This was corrected by preparing only small quantities of barium chloride to provide for fresh clear solutions for each set of determinations.

TABLE II

TUBIDIMETRIC SULFATE CALIBRATION CURVE DATA

Standard Sulfate ml	Water ml	Sulfate ppm	Absorbance Average	Reliability ppm
2.0	48.0	4.5	0.068	±0.2
4.0	46.0	9.0	0.202	±0.4
6.0	44.0	13.6	0.323	±0.7
8.0	42.0	18.1	0.410	±0.9
10.0	40.0	22.6	0.644	±1.1
12.0	38.0	27.1	0.785	±1.3
14.0	36.0	31.6	0.93 ⁺	±1.6

Most of the points on the graph lie on a straight line. The origin of the line does not lie on zero parts per million. This is due to the fact that the solubility product of barium sulfate at 20°C is 2.2 parts per million, so there is no chance for a zero reading. There are several points that do not lie on the line. These points are due to an unknown barium sulfate phenomenon. This has been recorded by several people,⁸ but considering the accuracy, the points are assumed to lie on the line.

The actual plot of barium sulfate curve has an initial slope similar to Figure 11, but at midrange the slope deviates.

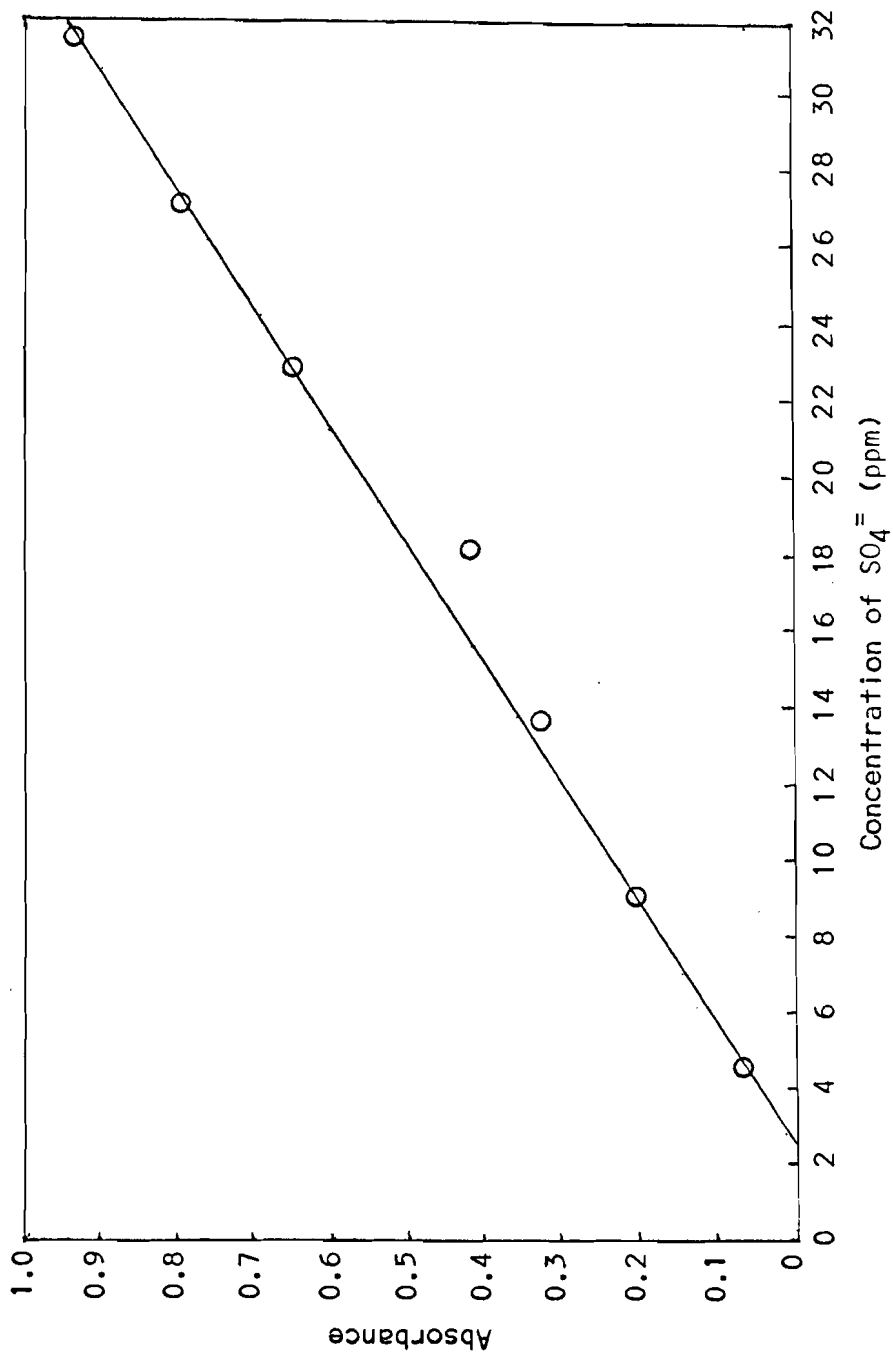


FIGURE 2

CALIBRATION CURVE FOR DETERMINATION OF SULFATE ION

CHAPTER III

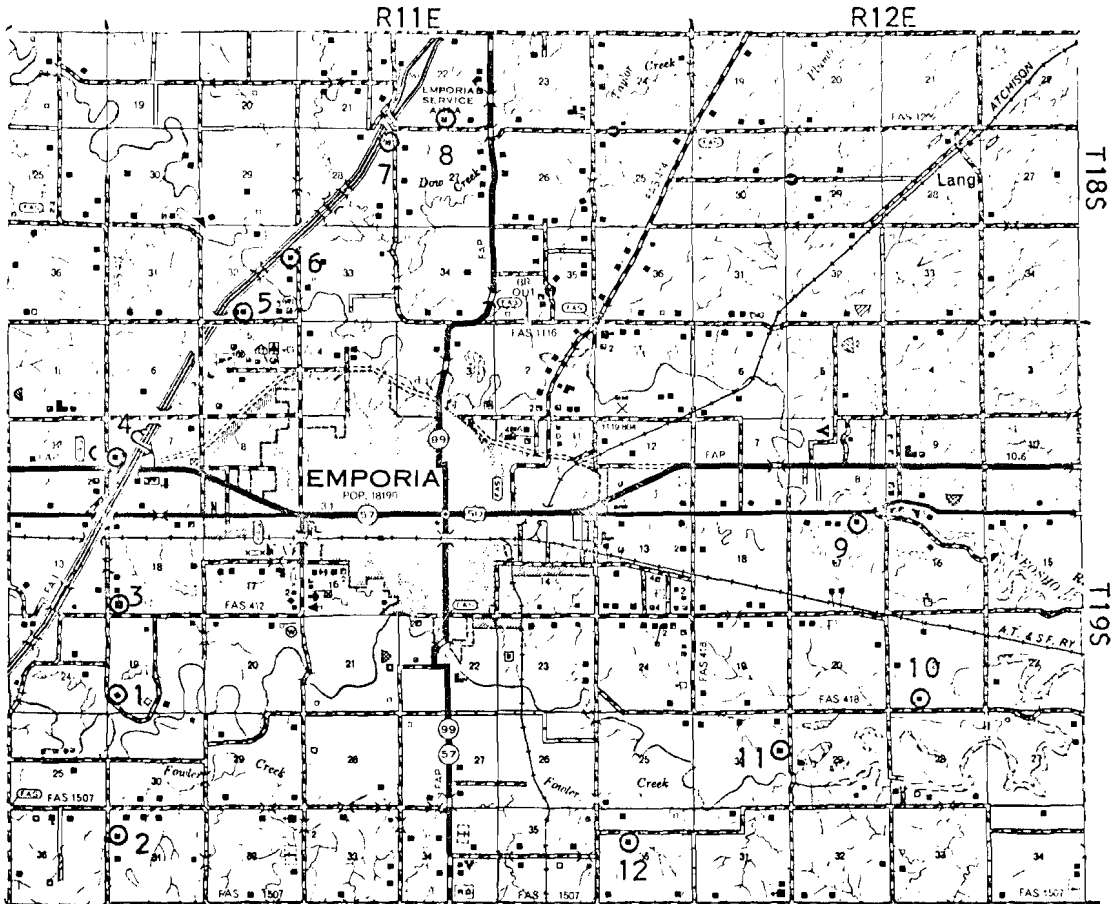
DATA AND DATA ANALYSIS

The map (Figure 2) shows the positions of the wells. The number in front of each well number is used in the following material as a shortened form of the standard well numbers. The standard well numbers used in this paper give the location of wells according to the following formula: township, range section, 160-acre tract within that section, and the 40-acre tract within that quarter section. The 160-acre and 40-acre tracts are designated a, b, c, and d in a counterclockwise direction beginning in the northeast quarter.¹

The data collected for this study was obtained by analysis of well water samplings taken at varying distances from the Cottonwood and Neosho Rivers. Tables 3 through 8 summarize the analytical data collected in this investigation. Table 9 lists the precipitation received in the Emporia area during the sampling period (January 28 through March 31, 1971) as reported by the Federal Aviation Administration Weather Monitor.

Investigation of Tables 3, 5, and 7 reveal the water type of well 1 to be calcium bicarbonate. This can be accounted for by dissolved limestone. The well contains only minor amounts of permanent hardness. It is of average depth (30 feet) and lies about 150 yards from the Cottonwood River. The consistency of the ionic content tends to show that even with moisture change, there was no noticeable change for the aquifer tapped by this well.

FIGURE 3
WELL LOCATIONS



Well Numbers

1. 19-11-19cb
2. 19-11-31bc
3. 19-11-18cc
4. 19-11-7bc
5. 18-11-32ad
6. 18-11-32cd
7. 18-11-28aa
8. 18-11-22dc
9. 19-12-17ab
10. 19-12-21cd
11. 19-11-30ad
12. 19-11-36bd

TABLE 3

DATA FROM WELLS LOCATED UPSTREAM FROM EMPORIA

Well Number	Sample Number	Temperature of H ₂ O °C _(a)	Acidity pH _(b)	Conductivity micromhos _(c)	Chloride ppm _(d)	Chloride milliequiv _(e)
1	1	*	6.8	925	***	***
	2	9.1	6.8	920	***	***
	3	11.9	7.0	905	***	***
2	1	*	7.2	2660	103	2.90
	2	12.4	7.2	2830	113	3.20
	3	12.0	6.9	2900	99	2.79
3	1	*	6.8	550	236	6.66
	2	16.6	6.8	710	235	6.65
	3	17.4	6.7	640	***	***
4	1	14.0	7.1	1105	73	2.06
	2	12.8	6.9	1080	78	2.22
	3	14.0	6.7	1080	73	2.06
5	1	3.3	7.3	1620	69	1.97
	2	4.7	6.9	1810	123	3.48
	3	8.4	7.2	1890	170	4.80
6	1	11.1	7.0	1015	191	5.39
	2	**	**	**	**	**
	3	**	**	**	**	**
7	1	12.3	7.1	786	36	1.02
	2	12.3	6.9	758	41	1.16
	3	17.0	7.1	780	39	1.10
8	1	14.5	6.8	990	89	2.50
	2	22.5	6.9	960	84	2.37
	3	19.3	6.6	970	86	2.43

Sample Number

(a) $\pm 0.05^{\circ}\text{C}$ (b) ± 0.05 units(c) ± 5 micromho(d) ± 5 ppm(e) ± 0.14 milliequiv.

* No thermometer

** No sample

*** Negligible

1 - January 28, 1971

2 - March 5, 1971

3 - March 31, 1971

TABLE 4

DATA FROM WELLS LOCATED DOWNSTREAM FROM EMPORIA

Well Number	Sample Number	Temperature of H ₂ O °C(a)	Acidity pH(b)	Conductivity micromhos(c)	Chloride ppm(d)	Chloride milliequiv(e)
9	1	12.6	7.2	1025	***	***
	2	14.0	6.7	830	***	***
	3	17.0	6.6	825	***	***
10	1	10.2	7.0	697	69	1.95
	2	**	**	**	**	**
	3	14.1	6.7	1175	86	2.43
11	1	13.0	7.0	748	40	1.13
	2	14.4	6.9	850	42	1.18
	3	16.1	6.7	835	43	1.21
12	1	5.3	7.0	295	***	***
	2	5.4	7.0	320	***	***
	3	9.4	6.9	330	***	***

Sample Number

(a) $\pm 0.05^{\circ}\text{C}$ (b) ± 0.05 units(c) ± 5 micromhos(d) ± 5 ppm(e) ± 0.14 milliequiv.

** No sample

*** Negligible

1 - January 28, 1971

2 - March 5, 1971

3 - March 31, 1971

TABLE 5

WATER HARDNESS DATA FROM WELLS LOCATED UPSTREAM FROM EMPORIA

Well Number	Sample Number	Ca ⁺² ppm	Mg ⁺² ppm	HCO ₃ ⁻ ppm	SO ₄ ⁼ ppm
1	1	200±2	6±3	611±2	32± 1.6
	2	211±2	3±5	620±2	19± 0.9
	3	221±2	0±5	617±2	14± 0.7
2	1	447±2	2±5	312±3	640±30.
	2	523±2	2±5	329±3	318±24.5
	3	590±2	0±5	370±3	312±24.5
3	1	108±3	2±5	310±3	38± 1.5
	2	152±3	0±5	487±2	9± 0.4
	3	160±3	1±5	485±2	10± 0.5
4	1	182±3	6±3	386±3	71± 4.5
	2	187±3	0±5	411±3	32± 1.6
	3	196±3	1±5	409±3	19± 0.9
5	1	270±2	4±4	373±3	250±12.5
	2	345±2	1±5	341±3	97± 4.8
	3	578±2	1±5	341±3	84± 4.2
6	1	175±3	4±4	378±3	100± 5.0
	2	**	**	**	**
	3	**	**	**	**
7	1	87±4	3±5	388±3	26± 1.2
	2	91±4	2±5	413±3	12± 0.6
	3	94±4	1±5	373±3	11± 0.5
8	1	103±3	5±3	379±3	39± 2.0
	2	107±3	1±5	408±3	16± 0.8
	3	116±3	0±5	382±3	14± 0.7

Sample Number

** No sample

1 - January 28, 1971

2 - March 5, 1971

3 - March 31, 1971

TABLE 6

WATER HARDNESS DATA FROM WELLS LOCATED DOWNSTREAM FROM EMPORIA

Well Number	Sample Number	Ca ⁺² ppm	Mg ⁺² ppm	HCO ₃ ⁻ ppm	SO ₄ ⁼ ppm
9	1	158±3	2±5	456±2	77±4.7
	2	183±3	4±4	538±2	17±0.8
	3	198±3	1±5	547±2	15±0.7
10	1	168±3	3±5	370±3	106±5.3
	2	**	**	**	**
	3	162±3	1±5	459±2	21±1.0
11	1	172±3	4±4	502±2	41±2.0
	2	172±3	6±3	504±2	17±0.8
	3	184±3	1±5	502±2	14±0.7
12	1	70±4	3±5	212±3	10±1.0
	2	63±4	1±5	185±3	8±0.4
	3	70±4	2±5	202±3	7±0.3

Sample Number

** No sample

1 - January 28, 1971

2 - March 5, 1971

3 - March 31, 1971

TABLE 7

HARD WATER DATA FROM WELLS LOCATED UPSTREAM FROM EMPORIA

Well Number	Sample Number	Ca ⁺² milliequiv.	Mg ⁺² milliequiv.	HCO ₃ ⁻ milliequiv.	SO ₄ ⁼ milliequiv.
1	1	9.98±0.05	0.50±0.24	10.01±0.03	0.66±0.03
	2	10.52±0.05	0.24±0.41	10.16±0.03	0.40±0.02
	3	11.04±0.05	0.04±0.41	10.12±0.03	0.29±0.02
2	1	24.30±0.05	0.16±0.41	5.11±0.05	13.32±0.63
	2	26.08±0.05	0.16±0.41	5.39±0.05	6.62±0.51
	3	29.44±0.05	0.04±0.41	6.06±0.05	6.71±0.51
3	1	5.38±0.07	0.50±0.41	5.08±0.05	1.48±0.03
	2	7.56±0.07	0.04±0.41	7.99±0.03	0.19±0.01
	3	8.00±0.07	0.08±0.41	7.95±0.03	0.21±0.01
4	1	9.08±0.07	0.16±0.24	6.33±0.05	0.80±0.09
	2	9.32±0.07	0.04±0.41	6.71±0.05	0.67±0.03
	3	9.76±0.07	0.12±0.41	6.30±0.05	0.40±0.02
5	1	13.48±0.05	0.32±0.33	6.11±0.05	5.20±0.26
	2	17.20±0.05	0.12±0.41	5.59±0.05	2.02±0.10
	3	28.82±0.05	0.12±0.41	5.59±0.05	1.75±0.87
6	1	8.74±0.07	0.32±0.33	6.20±0.05	2.08±0.10
	2	**	**	**	**
	3	**	**	**	**
7	1	4.34±0.10	0.24±0.41	6.36±0.05	0.54±0.02
	2	4.56±0.10	0.16±0.41	6.78±0.05	0.25±0.01
	3	4.68±0.10	0.12±0.41	6.10±0.05	0.23±0.01
8	1	5.14±0.07	0.42±0.24	6.21±0.05	0.80±0.04
	2	5.36±0.07	0.08±0.41	6.30±0.05	0.33±0.02
	3	5.80±0.07	0.04±0.41	6.26±0.05	0.29±0.02

Sample Number

** No sample

1 - January 28, 1971

2 - March 5, 1971

3 - March 31, 1971

TABLE 8

WATER HARDNESS DATA FROM WELLS LOCATED DOWNSTREAM FROM EMPORIA

Well Number	Sample Number	Ca ⁺² milliequiv.	Mg ⁺² milliequiv.	HCO ₃ ⁻ milliequiv.	SO ₄ ⁼ milliequiv.
9	1	7.88±0.07	0.16±0.41	7.47±0.03	1.60±0.10
	2	9.12±0.07	0.36±0.33	8.82±0.03	0.35±0.02
	3	9.88±0.07	0.12±0.41	8.97±0.03	0.31±0.02
10	1	3.38±0.07	0.24±0.41	6.06±0.05	2.20±0.11
	2	**	**	**	**
	3	8.08±0.07	0.12±0.41	7.52±0.03	0.44±0.02
11	1	8.58±0.07	0.32±0.33	8.23±0.03	0.86±0.04
	2	8.56±0.07	0.48±0.25	8.27±0.03	0.35±0.02
	3	9.20±0.07	0.08±0.41	8.23±0.03	0.29±0.02
12	1	3.50±0.10	0.24±0.41	3.47±0.05	0.42±0.02
	2	3.16±0.10	0.12±0.41	3.03±0.05	0.17±0.01
	3	3.48±0.10	0.16±0.41	3.31±0.05	0.15±0.01

Sample Number

** No sample

1 - January 28, 1971

2 - March 5, 1971

3 - March 31, 1971

TABLE 9

PRECIPITATION IN THE EMPORIA AREA
 FROM JANUARY 28, THROUGH MARCH 31, 1971, AS REPORTED BY
 THE FEDERAL AVIATION ADMINISTRATION WEATHER MONITOR

Date	Inches of Rainfall	Date	Inches of Rainfall
January 28	0.00	March 1	trace
29	0.00	2	0.00
30	trace	3	0.00
31	trace	4	0.00
February 1	0.01	5	0.00
2	0.00	6	0.00
3	0.00	7	0.00
4	0.40	8	0.00
5	0.01	9	0.06
6	0.00	10	0.00
7	0.00	11	0.00
8	0.00	12	0.00
9	0.00	13	0.00
10	0.00	14	trace
11	0.06	15	0.00
12	0.00	16	0.00
13	0.00	17	0.00
14	0.00	18	trace
15	0.00	19	trace
16	0.00	20	0.00
17	0.00	21	0.00
18	0.26	22	0.00
19	trace	23	0.00
20	0.00	24	0.20
21	0.56	25	trace
22	0.23	26	0.00
23	0.00	27	0.00
24	0.00	28	0.00
25	0.00	29	0.00
26	0.00	30	0.00
27	0.00	31	0.00
28	0.08		

The water type of well 2 (Tables 3, 5, and 7) was calcium bicarbonate and sulfate. This was the hardest of the waters analyzed. The well was located to the south of the terrace gravel and alluvium. The well was of the low water productivity type so the slower moving water may collect more minerals.

The water type of well 3 (Tables 3, 5, and 7) was primarily calcium bicarbonate. The first two samples yielded a high chloride content, but this disappeared almost entirely for the third sample. The calcium and bicarbonate increases were constantly in a ratio of 1:1, showing the increase by more dissolved limestone.

The water type of well 4 (Tables 3, 5, and 7) was calcium bicarbonate. There was a relatively constant chloride concentration with some sulfate present. The changes in the sample's ionic content did not correlate with precipitation records (Table 9).

The water type of well 5 (Tables 3, 5, and 7) was a mixture of calcium bicarbonate, sulfate, and chloride. There is no apparent reason for the great influx of calcium ion or the erratic fluctuation of the relatively high concentration of the sulfate and chloride. The well is located off the Neosho river terrace gravels. It is about 30 feet deep and a low productivity well.

The water type of well 6 (Tables 3, 5, and 7) was a mixture of calcium bicarbonate, sulfate, and chloride. The reason for the one sampling is that the occupants of the house at which the samples were taken were not at the house during the day of samplings or 3 subsequent times.

The water type of well 7 (Tables 3, 5, and 7) was calcium bicarbonate. There was little permanent hardness found in this water. The

well was being used during each of the samplings. The samples were taken after 200 to 500 gallons of water had been discharged. The small changes in concentration may have been due to the inflow of surrounding water.

The water type of well 8 (Tables 3, 5, and 7) was calcium bicarbonate. It is the sole source of water for a trailer park located north of Emporia. The lack of significant changes for the data could be due to the high productivity of the well.

The water type of well 9 (Tables 4, 6, and 8) was calcium bicarbonate. One reason for increased calcium bicarbonate content could be an increased solubility with the increased water temperature. The well is only 50 yards from the Neosho River.

The water type of well 10 (Tables 4, 6, and 8) was calcium bicarbonate. There was a marked increase in calcium and bicarbonate over the span of time. The first sampling indicated a relatively high sulfate content. The reason for the lack of a second sample was that at that time the quarter mile driveway leading to the farmhouse was blocked by mud and the farmer was not at home.

The water type of well 11 (Tables 4, 6, and 8) was calcium bicarbonate. The only noticeable change in ionic concentrations was a drop in sulfate concentration.

The water type of well 12 (Tables 4, 6, and 8) was calcium bicarbonate. This well was located south of Emporia on a hill. The well produces the softest water of all the wells sampled.

The individual well analysis shows that the predominant ions present in the waters are calcium and bicarbonate. Assuming the source of

the calcium to be attributed to be only dissolved limestone, there should be an equal number of equivalents of bicarbonate present. A plot of milliequivalents of calcium vs. milliequivalents of bicarbonate should yield a straight line (Figure 3). The experimental data from this study shows that upstream from Emporia and just off the south side of the terraces of the respective rivers, there is an increase in calcium which shows no increase in bicarbonate ion. The reasons for these differences are not evident from the data collected during this study. The remainder of the sample points lie on or near the line.

There is a characteristic of wells several miles north of the rivers on the upstream side of Emporia. They have between 6.0 and 6.8 milliequivalents of bicarbonate. The calcium concentration for these wells differ in that well 4 has as much calcium as most of the wells. Wells 7 and 8 have lower calcium concentrations. More data will need to be collected before general conclusions would be warranted regarding chloride ion. The chloride content ranged from a lower limit undetectable by the method used (below 1 milliequivalent) to an upper limit of 6.66 milliequivalents.

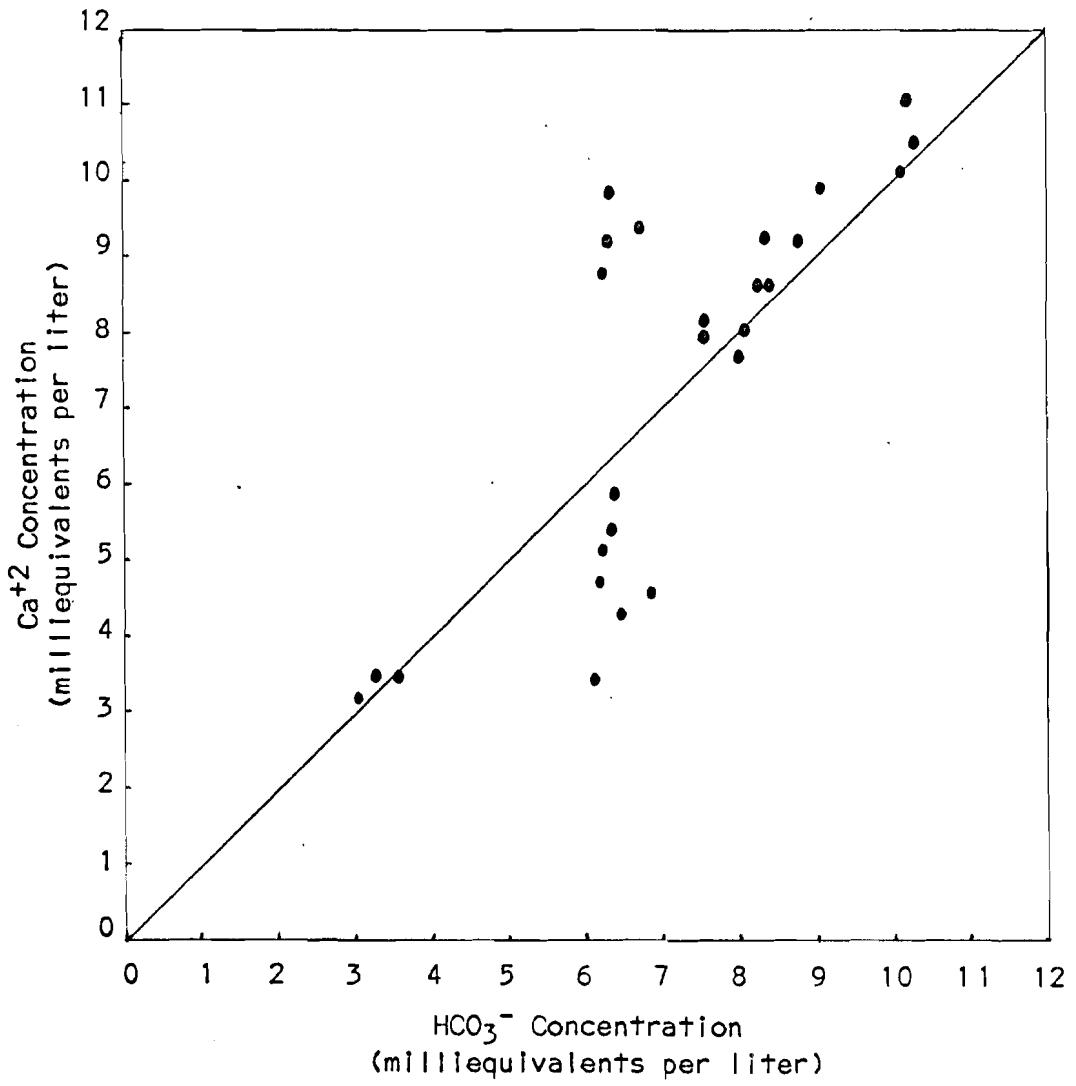


FIGURE 4

CONCENTRATION OF Ca^{+2} VS. CONCENTRATION OF HCO_3^-

CHAPTER IV

DISCUSSION

The purpose of this investigation was to complete the preliminary analysis of ground water in the vicinity of Emporia, Kansas, and to determine if the terrain on the upriver and downriver sides of Emporia would yield a decrease or increase of the hardness mineral content. The data collected infers that the predominant ions detected in this study were calcium and bicarbonate. These ions would be present in water found running through beds of limestone. Limestone is the most common bedrock in the area, so any ground water flowing in this vicinity should contain varying amounts of calcium and bicarbonate as controlled by temperature, water velocity, acidity, etc. The other ions tested in this study appear to have been due to sporadic contamination of the ground waters coming from many possible sources.

The multiple samplings helped in evaluation of changes in ionic concentrations. The data shows some possible trends as to ion concentration differences. While most wells showed slight changes as to total ion concentration, most wells could be classified as to type hardness based on $\text{Ca}^{+2}/\text{HCO}_3^-$ ratios. More extensive studies will be required to draw a definite conclusion as to the meaning of the data concerning sources of the other ions investigated. Differences in ion content for the two watersheds were encountered in this study. A better understanding of the source of ions would probably have been obtained by more extensive monitoring of wells.

The problem investigated in this study has importance in that it is the most extensive analysis of ground water in the Emporia area.

BIBLIOGRAPHY

BIBLIOGRAPHY

- (1) O'Connor, Howard G. Geology, Mineral Resources, and Ground Water Resources of Lyon County, Kansas. Part 3. Lawrence: University of Kansas Publications, 1953.
- (2) American Public Health Association et al., comp., Standard Methods for the Examination of Water and Industrial Wastes. Thirteenth Edition. New York: American Health Association, Inc., 1966.
- (3) Skoog, Douglas A. and Donald M. West. Fundamentals of Analytical Chemistry. Second Edition. New York: Holt, Rinehart, and Winston, Inc., 1969.
- (4) Kolthoff, I. M. and E. B. Sandell. Textbook of Quantitative Inorganic Analysis. Third Edition. New York: MacMillan, Inc., 1953.
- (5) Meloan, Clifton and Robert W. Kiser. Problems and Experiments in Instrumental Analysis. Columbus: Merrill Publishing, 1966.
- (6) Rosin, Joseph. Reagent Chemicals and Standards. Fourth Edition. Princeton: D. Van Nostrand, 1961.
- (7) Golterman, H. L. Methods for Chemical Analysis of Fresh Water. IBP Handbook No. 8, London: Blackwell Scientific Publications, 1970.
- (8) Liteanu, Candin and Harold Lingner. Talanta, 17:1045, 1970.