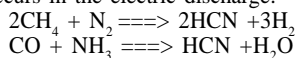


dicyanoacetylene. Taking into consideration the data received that further elucidate the formation of hydrocyanic acid from DND under the laboratory conditions, one can assume, that  $N_2$  is first chemisorbed with the dissociation into atoms on the DND surface followed by the formation of nitryl groups, which are subsequently hydrogenated with  $H_2$  (probably as well as by atomic hydrogen) to produce hydrocyanic acid.

The curvature of the surface is extremely high due to the nanosize of diamonds and the latter favours the dissociation of the adsorbed diatomic molecules of hydrogen into atoms.

The observed formation of a hydrocyanic acid under soft conditions provides additional data for the consideration of the initial stages of the genesis of carbon compounds in the Universe. So, according to the classic theory of the life origin on the Earth (MILLER 1953), the formation of HCN occurs in the electric discharge:



Considering the data regarding the formation of hydrocyanic acid under mild conditions provides a new perspective on this theory.

Further, the structure of the atmospheres of giant-planets in our Solar system can include ammonia and methane in a molar ratio approximately 1:1 (table 1) (one must take into account the composition of aerosols).

**Table 1.** The structure of the gas atmospheres of planets-giants of Solar system

Planet	Composition of atmosphere [http://nssdc.gsfc.nasa.gov/planetary]
<b>Jupiter</b>	$H_2$ - 89.8%; He - 10.2% impurities (ppm): $CH_4$ - 3000; $NH_3$ - 260; HD - 28; $C_2H_6$ - 5.8; $H_2O$ - ~4 Aerosols: solid $NH_3$ , $H_2O$ , $NH_4HS$
<b>Saturn</b>	$H_2$ - 96.3%; He - 3.25% impurities (ppm): $CH_4$ - 4500; $NH_3$ - 125; HD - 110; $C_2H_6$ - 7 Aerosols: solid $NH_3$ , $H_2O$ , $NH_4HS$
<b>Neptune</b>	$H_2$ - 80.0%; He - 19.0%; $CH_4$ 1.5% impurities (ppm): HD - ~192; $C_2H_6$ - ~1.5 Aerosols: solids $NH_3$ , $H_2O$ , $NH_4HS$ , $CH_4$ (?)
<b>Uranus</b>	$H_2$ - 82.5%; He - 15.2%; $CH_4$ - ~2.3% impurities (ppm): HD - ~148 Aerosols: solids $NH_3$ , $H_2O$ , $NH_4HS$ , $CH_4$ (?)

Precisely the same parity between these compounds is observed under the reduction of a hydrocyanic acid with hydrogen  $HCN + 3H_2 = CH_4 + NH_3$ . In view of these data it is possible to hypothesise that in the first stage of formation of giant-planets of the solar system there was hydrocyanic acid which was subsequently converted to ammonia and methane (VERESHCHAGIN 2003). The HCN was originally formed from ultradisperse carbon, hydrogen and nitrogen.

Therefore, the products of the carbon stars explosion may contain a plenty of the various carbon substances formed in the reactions of a primary carbon, – hollow diamond nanoparticles and the products of their hydrogenation: fullerenes, polycyclic structures, hydrocyanic acid, ammonia, methane. Besides, the DND at temperatures higher than 1273 K are capable to be graphitized.

Thus, detonation nanodiamonds may be hypothesised as the primary state of carbon in the Universe.

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## Special section: Microscale Science Sección especial: Ciencia en microescala

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### Determination of the hardness of water by a microscaled EDTA titration

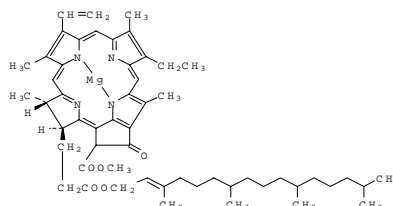
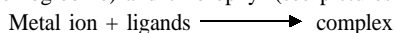
#### INTRODUCTION

Most of the water that we drink contains positive ions (cations) and negative ions (anions). The most common cations in water are  $Na^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$ . These ions are the substituents of most of the earth's rocks, and during solubility they will always be found in rivers, lakes, and the ocean.

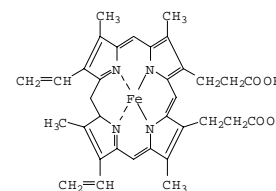
When water contains these two ions it is called "hard water", and without these ions the term is "soft water" (e.g., rain water).

#### How is the "hardness" of water determined?

To determine the **amounts** of  $Ca^{2+}$  and  $Mg^{2+}$  (hardness) in water, a known technique called "complexometric titration" is used. **Complexes** are compounds that are produced when an ion metal reacts with molecules or ions (ligands) that have a tendency to "contribute" electrons. An example of two well known complexes in our everyday life are hem (hemoglobine) and chlorophyll (see pictures below).

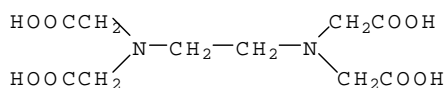


**Chlorophyll**



**hem**

One of the most powerful ligands which is used to form complexes with many kinds of ion metals is EDTA (ethylene diamine tetra acetic acid).

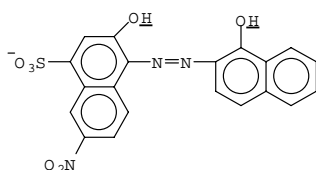


**EDTA**  
Ethylenediaminetetraacetic acid

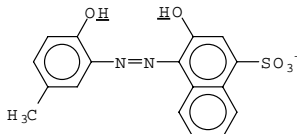
Each EDTA molecule has 6 ligands (4 carboxy groups and 2 nitrogen atoms), enabling it to form 6 coordinative bonds to a metal ion. The complexes thus formed are very stable and have stability constants in orders of magnitude of  $10^{10}$ - $10^{25}$ .

#### Indicators in EDTA titrations

Two of the indicators in complexometric (EDTA) titrations are Eriochrome black T (Erio-T) and Calmagite. In pH's between 7-11.5 these indicators are blue in color when they are free, and wine-red in color when they are complexed with ion metals. In the **direct titration** of an ion metal with EDTA in the presence of the indicator, the endpoint is determined when the initial red color changes to blue.  $\text{Mg}^{2+}$  can be determined with EDTA directly, but  $\text{Ca}^{2+}$  has no appropriate indicator (it forms an unstable complex with either Erio-T or Calmagite). Therefore, a **substitution titration** is used for  $\text{Ca}^{2+}$ . In this titration a small amount of Mg-EDTA is added to the  $\text{Ca}^{2+}$ . The calcium ion replaces the magnesium ion in complexation with EDTA and the behaviour of the color becomes the same as that in the direct titration (from wine-red to blue).



**Eriochrome Black T**  
 $\text{pK}_2 = 6.3 \quad \text{pK}_3 = 11.6$



**Calmagite**  
 $\text{pK}_2 = 8.1 \quad \text{pK}_3 = 12.4$

## EXPERIMENTAL

### Materials and equipment



Figure 1

- A standard solution of EDTA (as the dianion salt)  $5 \times 10^{-3}\text{M}$ .
- A microburette (made of a 2 mL syringe) with a stopcock with a yellow tip on its end (see figure 1).
- Plastic wellplates "6" (each well can contain 3 mL).
- An automatic delivery pipette (optional).
- Small magnetic bars (or small pieces of straw for mixing).
- A magnetic stirrer.
- A standard  $\text{Ca}^{2+}$  solution (500mg/L)
- Calmagite (0.05% in water), Erio-T 0.4% in ethanol
- A Mg-EDTA solution (made by the exact titration of  $\text{Mg}^{2+}$  with EDTA with Erio-T as the indicator).

A buffer solution, pH=10 (made from an ammonia solution).

### Microscaled titration: General procedure

1. Fill the syringe with the standard EDTA solution by pumping. Close the stopcock.
2. Deliver 1 mL of the standard  $\text{Ca}^{2+}$  solution to one well of the wellplate 6. Add 2 drops of the buffer solution and 1 drop of the indicator, Calmagite. Add also one drop of the Mg-EDTA solution. The solution will turn red.
3. Titrate the solution in the wellplate by adding drops of EDTA from the syringe to the wellplate (figure 2). Mix the contents of the wellplate. Continue the titration until the color changes to blue. Count the number of drops needed to complete the titration.
4. Repeat the titration with other samples of sea water and different brands of mineral water, etc.
5. Calculate the hardness of the titrated samples and compare it to the advertized values.

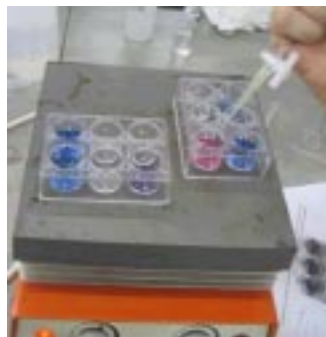


Figure 2

## RESULTS AND CALCULATIONS

The hardness of a sample (in mg/L) is calculated using the following equation:

$$\text{hardness (mg/L)} = 500 \cdot \frac{\text{nd(sample)}}{\text{nd(standard)}} \cdot \frac{\text{v(standard)}}{\text{v(sample)}}$$

- nd(sample) = number of drops used to titrate the sample
- nd(standard) = number of drops used to titrate the standard
- v(sample) = volume of titrated sample
- nd(standard) = volume of titrated sample

Typical results are given in the following table:

	nd	v (mL)	Hardness (mg/L)
Standard $\text{Ca}^{2+}$ solution	77	1	500
The Mediterranean Sea water	37	0.1	2403
Faucet BIU water	40	1	260
Mineral water from Golan Heights	38	1	247

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