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Method of Investigation of Soil Contamination with Heavy Metals at the Sites of Explosions

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Abstract. The study evaluates the method of investigation of soil contamination with heavy metals at the sites of explosions. Results of method application were obtained. Soil samples were collected in location selected as the typical place were explosions take place for explosive objects destruction. For the qualitative and quantitative analysis of soil samples, the "KBr tablets" method was used. Obtained pellets were investigated with spectral-analytical installation created on the basis of infrared-spectrometer IKS-21 and thermal imager LAND-814. IR spectrometric research was carried out in the most informative spectral range of wavelengths of 7.5...14 μm. Proposed method of investigation of soil contamination with heavy metals at the sites of explosions allowed to identify presence of such metals as Al, Cu, Fe, Mg, Ni and Zn in soil samples of explosion site. Mg, Ni and Zn show stable presence in the soil of explosion site with low amount. Al, Cu and Fe we have seen sharp decrease of logarithmic transmittance value at the depth of 10…15 cm which means that these elements are accumulated at these depths of soil after explosions.

Introduction

With the widespread use of long-range artillery, attack and bomber aircraft, as well as missile weapons, the area of territories that are negatively affected during armed conflicts is growing significantly. It is practically impossible to limit the territorial impact of these types of weapons, in particular, on the environment. In recent years, the impact of armed conflicts on the natural environment has become the object of assessment in a global context, in particular, such impacts were assessed on the territory of Lebanon [1], Iraq [2], Afghanistan [3], Congo [4], Croatia [5], the Gaza Strip [6], Syria [7], etc.

According to the results of a study conducted by the Regional Ecological Center of Central and Eastern Europe regarding the impact of the 1999 armed conflict in Yugoslavia [8], the presence of craters from explosions, as well as damage to the soil structure, resulting in land degradation and the subsequent death of flora and fauna, was established. The remains of organic explosives and heavy metals also enter the soil. The latter are today one of the most dangerous pollutants, because due to their inorganic origin, they cannot be neutralized naturally [9–12]. Consequences of soil contamination with heavy metals are suppression of vital activities of representatives of flora [13–16] and fauna [17–21].

Modern studies of the soils of the lands of Ukraine demonstrate the same set of factors of negative influence [22]. Soils are the most contaminated by explosions. The relevance of the task of ensuring the environmental safety of objects contaminated by explosive substances is today undeniable for the world community [23]. The goal of activities in this direction should be to restore the lands of places contaminated by explosions, in particular, places of neutralization and destruction of ammunition.

Armed conflicts in the world lead to large-scale contamination of large territories of the states participating in the conflict with explosive objects. Report materials based on the results of studies of the environmental consequences of armed conflicts and the use of the specified tactics of warfare demonstrate common features of the impact on the lands subjected to shelling [8, 22]. One of the factors of negative impact on the soil is pollution and heavy metals, which due to their inorganic origin cannot be neutralized naturally [9]. At the same time, the concentrations may exceed the permissible limits, however, the possibilities of their detection in soil samples are significantly limited, since they require the use of complex laboratory equipment and the provision of appropriate conditions for conducting experiments.

There are studies on environmental impact of different types of emergencies, in particular, fire [24], nuclear power plant emergency [25], surface water degradation [26], nanomaterials overaccumulation [27], atmosphere pollution [28–30], etc. Different sorts of methods are proposed for detection of such impacts, in particular, for detection of pollution characteristics in atmosphere [31, 32], surface water bodies [33], wastes landfills [34], including pollution adjoined to emergency situations [35] and explosions [36]. However, it may be seen that such methods are not applicable for investigation soil pollution by heavy metals in case of explosion.

It is possible to solve the task of creating a methodology for the study of soil pollution by heavy metals in the places of explosions directly in the field using the method of infrared (IR) spectrophotometry, followed by a comparison of the obtained IR spectrum with an exemplary IR spectrum of the studied heavy metal [37]. Among material objects, there are no compounds that have a different structure, but the same IR spectrum, which makes it possible to identify the corresponding contamination in a soil sample by detecting separate bands of the IR spectrum characteristic of it. Thus, it becomes possible to determine the content of each of its individual components, in particular, heavy metals, from the IR spectrum of a soil sample.

The theory of construction of environmental protection technologies on the example of environmentally hazardous technical energy generating facilities consuming carbon-containing non-renewable fuels is represented in the monograph [38]. The theory and examples of developing of ecological safety management systems based on relevant environmental protection technologies, as the methodological basis for ensuring the legislative established level of environmental safety, are described in the source [39].

Materials and Methods

Contamination by heavy metals as a result of the explosion occurs in the surface layer of the soil, however, their migration deep into the soil layer is possible in the future. In connection with the above, soil sampling for research should be carried out to a depth of up to 30 cm with subsequent research of sections at different depths.

Soil samples were collected in location selected as the typical place were explosions take place for explosive objects destruction. The sampler was used to collect core samples of soil on the depth up to 30 cm. Obtained core samples were used for following selection of separate soil samples from soil surface layer (0 cm depth) and deeper layers (10, 15, 20, 25 and 30 cm depth) correspondingly.

For the qualitative and quantitative analysis of soil samples, the "KBr tablets" method was used. Obtained samples were processed in pellets with Potassium bromine (KBr) salt used as suspending medium [40]. Finely divided soil samples were thoroughly mixed with subsequent pressing into molds to obtain transparent tablets. This method allows to exclude most bands of the spectrum and control the concentration of the sample.

Obtained pellets were investigated with spectral-analytical installation created on the basis of infrared-spectrometer IKS-21 and thermal imager LAND-814 [41]. Optical scheme of spectral-analytical installation is shown at Fig. 1. Principle of action of spectral-analytical installation is shown at Fig. 2.

For spectroscopic studies, the IKS-21 spectrometer, improved by using a non-selective matrix of sensitive elements of the LAND-814 thermal imager, was used. This approach made it possible to qualitatively improve the sensitivity and spectral resolution of the system [41].

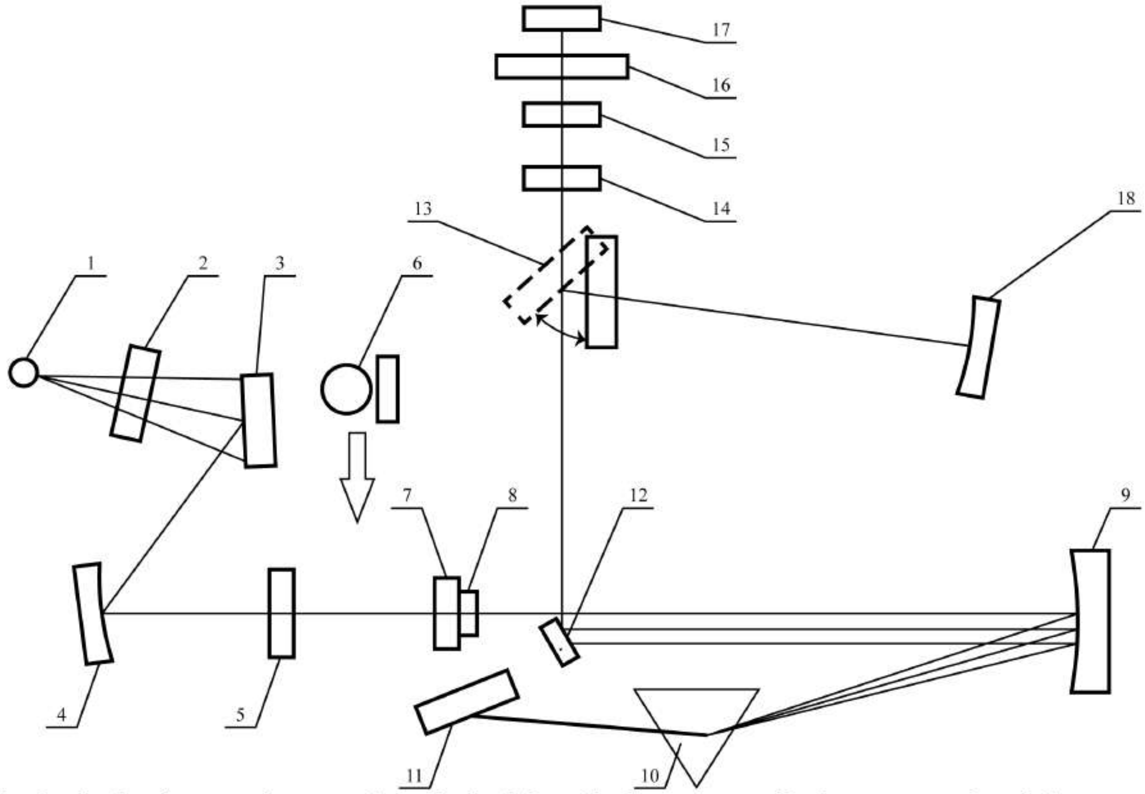

Fig. 1. Optical scheme of spectral-analytical installation: 1 – radiation source; 2 – inlet protective window of the illuminator; 3 – flat mirror; 4 – spheric mirror; 5 – outlet protective window of the illuminator; 6 – cuvette; 7 – aperture; 8 – inlet gap; 9 – extraaxial parabolic mirror; 10 – prism; 11 – Littrov's mirror or echelette replica; 12 – flat mirror; 13 – flat rotating mirror; 14 – outlet protective window of monochromator or filter; 15 – optical system of radiometer; 16 – full-scale Focal Plane Arrows (FPA) matrix of "looking" type; 17 – block of measurement results processing; 18 – single radiation receiver

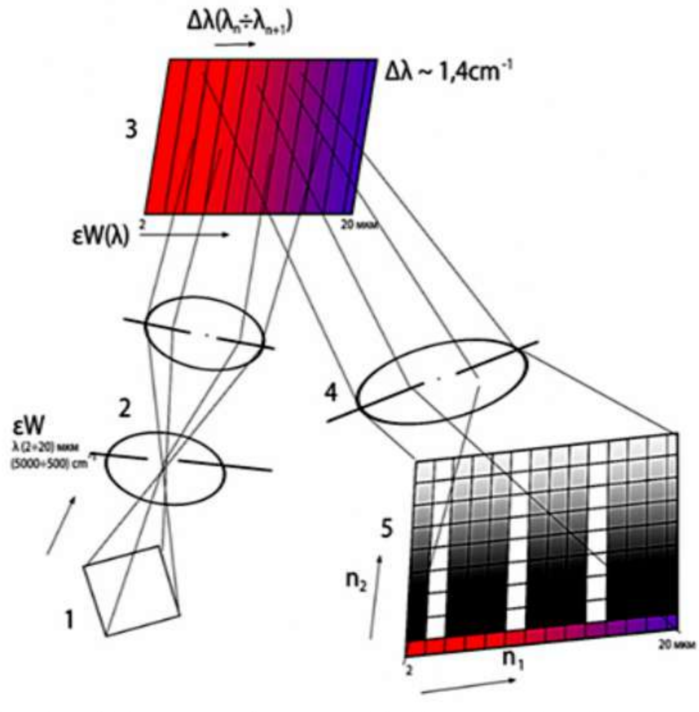

Fig. 2. Scheme of infrared radiation spectrum registration and visualization: 1 – radiation source; 2 – infrared optical system; 3 – dispersion block; 4 – infrared-toroidal optical system; 5 – full-scale Focal Plane Arrows (FPA) matrix of "looking" type

IR spectrometric research was carried out in the most informative spectral range of wavelengths of 7.5...14 μm. Its advantage is the location in it of the spectral maximum of the intrinsic radiation of terrestrial objects at a normal temperature of T~300 K, which corresponds to a wavelength of ~ 10 μm.

Comparison of obtained spectra with the etalon ones allows to identify composition of complex chemical compounds and separate specific components of it. For identification of the pollutants exposed by explosions of the ammunition we have used etalon spectra of Al_2O_3 (Fig. 3), MgO (Fig. 4) and $MgAl_2O_4$ (Fig. 5) together with those of the existing catalogs of IR spectra [37, 42]. Based on the results of the analysis of the absorption spectra of the studied sample and the reference spectrum, separate bands that are not affected by other components were determined for each component of the mixture.

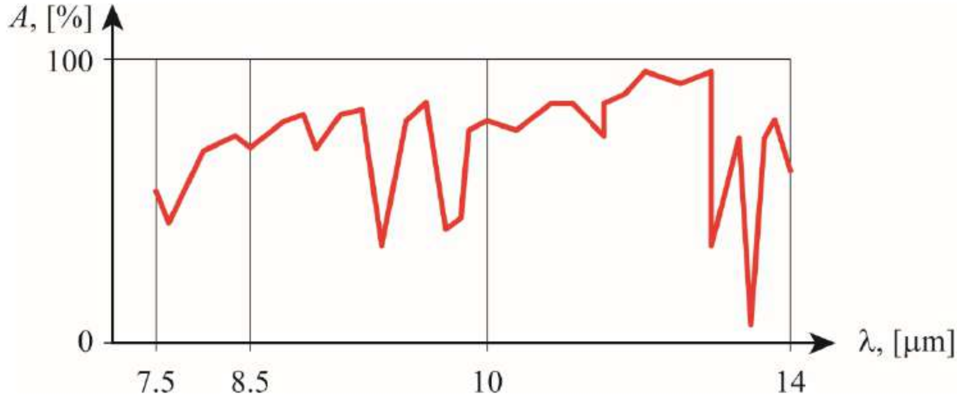

Fig. 3. Etalon spectrum of Al_2O_3

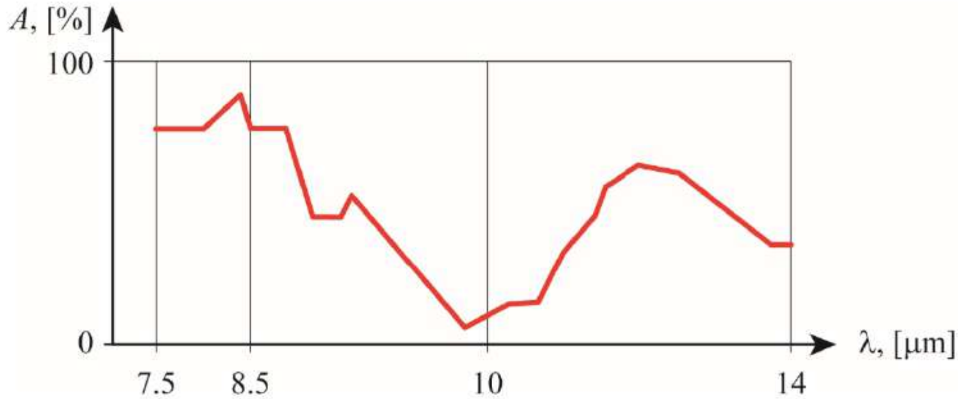

Fig. 4. Etalon spectrum of MgO

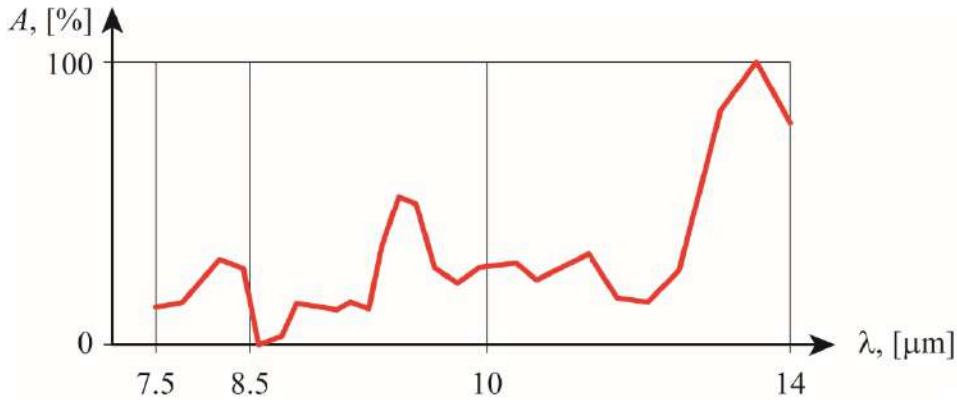

Fig. 5. Etalon spectrum of $MgAl_2O_4$

The value of the logarithmic transmittance of the studied sample was determined by the selected bands according to the formula [40]:

$$T = \lg (I / I_0), \quad (1)$$

where I_0 – intensity of falling radiation of a certain wavelength; I – intensity of the radiation that passed through the sample. In this case value $T = 1$ means no presence of investigated substance in the sample mixture and its decrease corresponds to raise of amount of investigated substance in the sample mixture.

Discussion

The results of the logarithmic transmittance evaluation for soil samples are shown in Table 1. Graphs of dependences of logarithmic transmittance value from depth of soil samples obtaining are shown on Fig. 6-13.

Table 1. Logarithmic transmittance values, obtained in experiment

Sample No,	1	2	3	4	5	6
Depth, [cm]	0	10	15	20	25	30
Sunstance	Logarithmic transmittance T					
Al_2O_3	0.740	0.699	0.319	0.640	0.767	0.667
MgO	0.699	0.682	0.640	0.683	0.682	0.767
$MgAl_2O_4$	0.667	0.767	0.598	0.685	0.740	0.718
FeO	0.640	0.319	0.685	0.682	0.683	0.767
Fe_2O_3	0.598	0.333	0.640	0.598	0.767	0.718
CuO	0.667	0.319	0.332	0.640	0.683	0.682
ZnO	0.682	0.767	0.640	0.683	0.740	0.718
NiO	0.767	0.685	0.682	0.767	0.683	0.683

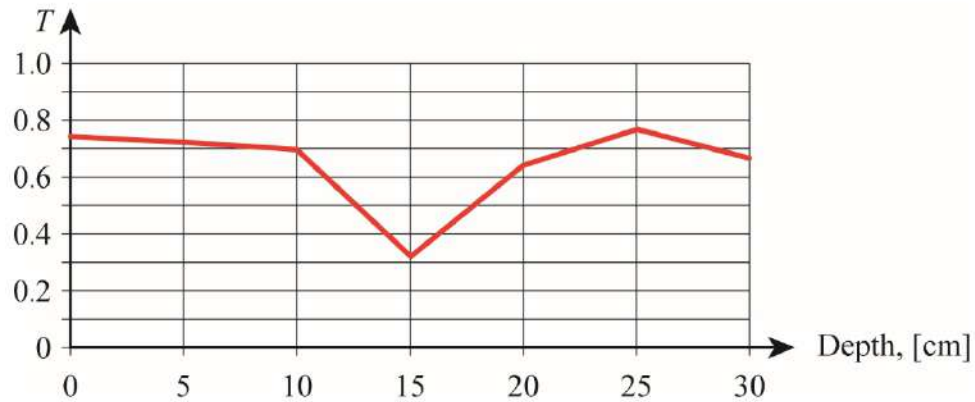

Fig. 6. Logarithmic transmittance value from depth of soil samples obtaining for Al_2O_3

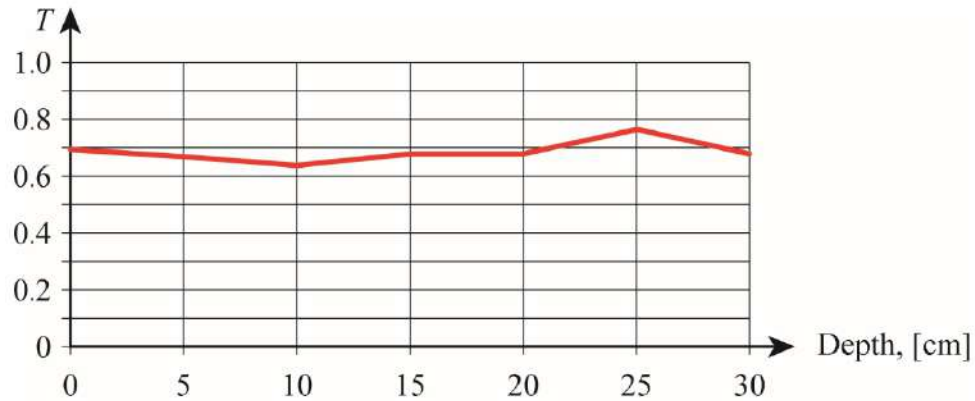

Fig. 7. Logarithmic transmittance value from depth of soil samples obtaining for MgO

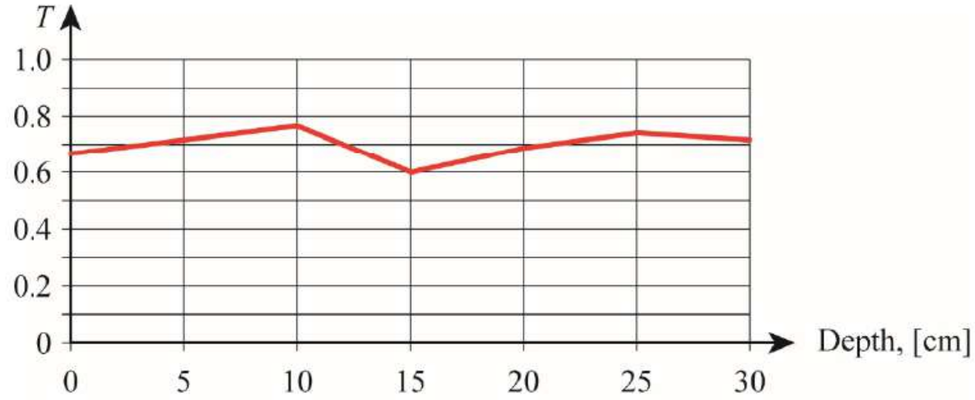

Fig. 8. Logarithmic transmittance value from depth of soil samples obtaining for $MgAl_2O_4$

Fig. 9. Logarithmic transmittance value from depth of soil samples obtaining for FeO

Fig. 10. Logarithmic transmittance value from depth of soil samples obtaining for Fe_2O_3

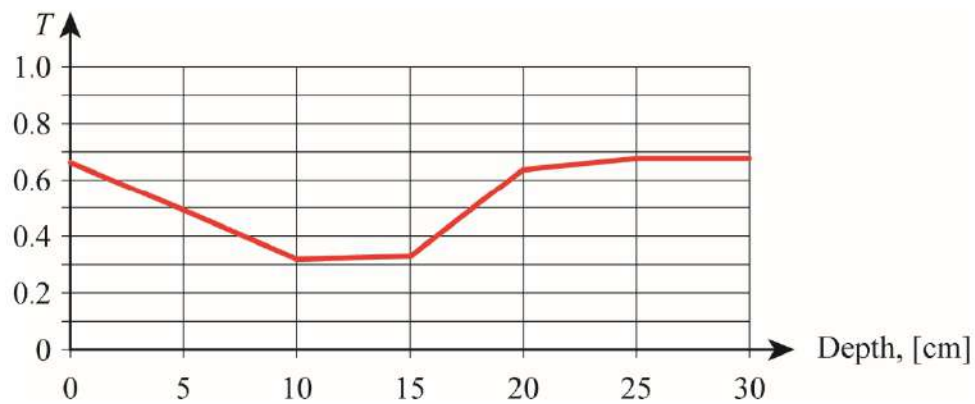

Fig. 11. Logarithmic transmittance value from depth of soil samples obtaining for CuO

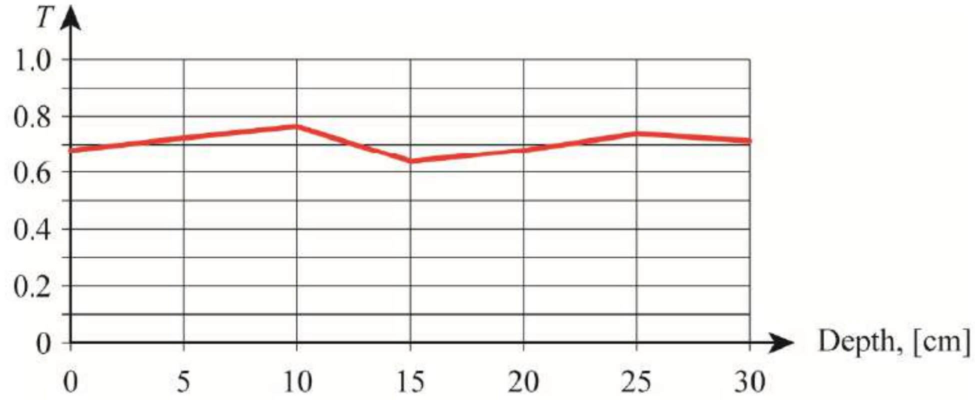

Fig. 12. Logarithmic transmittance value from depth of soil samples obtaining for ZnO

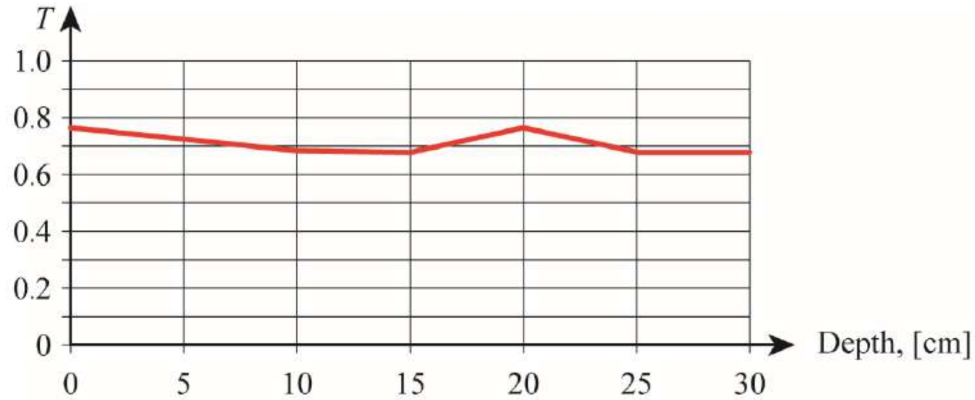

Fig. 13. Logarithmic transmittance value from depth of soil samples obtaining for NiO

Analysis if obtained results show that such metals as Mg, Ni and Zn show stable presence in the soil of explosion site. Instead for such metals as Al, Fe and Cu we have seen sharp decrease of logarithmic transmittance value at the depth of 10…15 cm which means that these elements are accumulated at these depths of soil after explosions.

Conclusions

The following conclusions were made from represented research:

1. Proposed method of investigation of soil contamination with heavy metals at the sites of explosions allowed to identify presence of such metals as Al, Cu, Fe, Mg, Ni and Zn in soil samples of explosion site.
2. Such metals as Mg, Ni and Zn show stable presence in the soil of explosion site with low amount. Instead for such metals as Al, Cu and Fe we have seen sharp decrease of logarithmic transmittance value at the depth of 10…15 cm which means that these elements are accumulated at these depths of soil after explosions.
3. Application of reference absorption spectra of the studied soil sample and the reference spectrum of different substances with separate bands not affected by other components allows to identify composition of complex chemical compounds and separate specific components of it.
4. IR spectrometric research provides the possibility of further improvement of the proposed methodology for the study of soil contamination by heavy metals in the places of explosions in the direction of the implementation of remote spectral sensing in field conditions.

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