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Detection of concealed and buried chemicals by using multifrequency excitations

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In this paper, we present a new type of concealed and buried chemical detection system by stimulating and enhancing spectroscopic signatures with multifrequency excitations, which includes a low frequency gradient dc electric field, a high frequency microwave field, and higher frequency infrared (IR) radiations. Each excitation frequency plays a unique role. The microwave, which can penetrate into the underground and/or pass through the dielectric covers with low attenuation, could effectively transform its energy into the concealed and buried chemicals and increases its evaporation rate from the sample source. Subsequently, a gradient dc electric field, generated by a Van De Graaff generator, not only serves as a vapor accelerator for efficiently expediting the transportation process of the vapor release from the concealed and buried chemicals but also acts as a vapor concentrator for increasing the chemical concentrations in the detection area, which enables the trace level chemical detection. Finally, the stimulated and enhanced vapors on the surface are detected by the IR spectroscopic fingerprints. Our theoretical and experimental results demonstrate that more than sixfold increase in detection signal can be achieved by using this proposed technology. The proposed technology can also be used for standoff detection of concealed and buried chemicals by adding the remote IR and/or thermal spectroscopic and imaging detection systems. © *2010 American Institute of Physics.* [doi:10.1063/1.3474651]

I. INTRODUCTION

In recent years, the quantization and identification techniques of concealed and buried chemicals and objects are critically needed for many applications such as monitoring hazardous underground chemicals for pollution and contamination control. Different techniques have been proposed for this purpose. However, these approaches only achieved limited successes due to the inherent limitations of each corresponding technique. For example, ground penetrating radars (GPRs) detect the buried objects by measuring the electric property discontinuity of the underground materials such as plastics or metals associated with the target.[1] Unfortunately, there is a fundamental tradeoff between the selectivity and the depth of the detection. The high selectivity requires high spatial resolution which can only be achieved with radar signals at high frequency but the high frequency radar signal has a poor ground penetration capability. The methods of mass spectrometry and ion-mobility spectroscopy have high sensitivity and selectivity but they require the collection of samples beforehand, which make them not suitable for real time standoff detection.[2] The combination of acoustic wave and the surface laser Doppler is another method for locating the buried objects.[3] However, similar to the case of GPR, to achieve high resolution imaging, high frequency acoustic waves have to be used, which has a poor penetration capability. Other techniques such as using millimeter wave and x-ray back scattering methods also suffer certain limitations. For example, to increase the penetration capability of x-ray, high energy radiations are needed, which introduces a potential health risk to people around it.

On the other hand, recently, it has been found that the emanated chemical vapors from the buried objects can provide a unique chemical "signature" which may be utilized for their identification with high specificity and accuracy. However, the main challenge of this approach comes from the fact that the vapors released from the buried sample is usually at very low level, which increases the difficulty of the detection.[4] Furthermore, several laser based approaches for detecting the trace levels of emanated chemical vapors have also been exploited, such as using the laser induced fluorescence effects in the UV region, commonly referred to as photofragmentation-fragment-detection spectrometry.[5,6] Nevertheless, the laser beam can only interact with the buried sample by using a fiber-optic cable based penetrometer due to the fact that a laser beam cannot directly penetrate into the soil. Another technique involves the use of time-consuming amplification of fluorescence quenching,[7] which makes them not suitable for real-time applications.

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To overcome the limitations of the existing techniques, in this paper, we present a new detection method by using multifrequency excitations, including gradient static electric field, microwave, and the near infrared radiation (NIR). Different frequency electric fields play different roles. The low frequency gradient electric field, generated from a Van De Graaff generator, is employed to accelerate the vapor evaporation process and to increase the concentration level at the detection areas. The microwave frequency is used to improve the buried chemical equilibrium vapor pressure and to heat up the buried polar chemicals. The NIR radiation is used to identify the "chemical signatures" based on the fact that the most molecules have the vibrational and the rotational energy state transitions in this optical spectral region. To validate this approach and verify its feasibility, the commonly used organic compound cyclohexanone $(CH_2)_5CO$ is selected as the material to be detected. The paper is organized in the following way: The detailed theoretical description of the proposed approach is presented in Sec. II. The simulation result is given in Sec. III. And, the experimental result is provided in Sec. IV. Finally, a brief conclusion is drawn in Sec. V.

II. THEORY

In this section, the basic theory is divided into three parts: (1) transportation of buried chemicals from underground to surface; (2) enhance chemical evaporation by microwave excitation; and (3) gradient dc field based vapor concentration and acceleration.

The transport behavior of the emanated chemical constituents from underground to the surface of soil is involved with multiple phase transition processes among vapor phase, aqueous phase, and solid phase, which is affected by the multiple environmental factors. First, a small portion of molecules in the buried chemicals possess enough heat energy to evaporate from the solid phase to the vapor phase. Second, if there is water in the soil, there is a possibility for the vapors to be dissolved into the water in the soil forming the aqueous phase. Both vapor and aqueous phase chemicals can be transported up from underground to the surface but with different mechanisms: the vapor phase chemical is transported up to the surface due to the barometric pressure changes whereas the aqueous phase is transported up to the surface by evapotranspiration and concentration gradients diffusion. In addition, during the transport process through the soil as the vapor or aqueous phase, there is also another chance for the emanated chemical to be adsorbed to soil particles forming the solid phase again, especially under dry soil condition. However, different from the previous two phases, the transport of the solid phase cannot be in the vertical motion but horizontal in the soil. In other words, chemical constituents in this phase cannot reach the soil surface directly by itself but can only be transported upward by transforming into other two phases under reversible partitioning reactions. Besides, it is also likely for them to be permanently bonded to the soil particles by chemisorption reactions.

A buried chemical model[8] has been developed to describe the behavior of emanated chemical signature, as mathematically given by

$$\frac{\partial c_t}{\partial t} = D_E \frac{\partial^2 c_t}{\partial z^2} - V_E \frac{\partial c_t}{\partial z} + \sigma, \tag{1}$$

where c_t is the total concentration of chemical in the soil, D_E and V_E are the effective diffusion and effective velocity, respectively. A more detailed description of each parameter's physics meaning is given by Ref. 8. Furthermore, the chemical decaying term is omitted in our description because it is not important for the real time detection system of this paper.

As aforementioned, although the transport of the emanated vapor to the soil surface can occur automatically based on the condition of the soil, the extremely low vapor concentration and the unacceptable long lagging time for the vapor to be released from the soil make it very challenging for the real time detection. On the other hand, it is well known that a higher vapor pressure of the chemical could result in a higher evaporation rate, which could accelerate the vapor transporting process to the surface, and thus increase the concentration of the detected chemical signatures. According to the definition in Wikipedia, the Clausius–Clapeyron relation that describes the relationship between the substance's vapor pressure and temperature can be written as

$$\frac{dP}{dT} = \frac{L}{T\Delta V}, \tag{2}$$

where dP/dT is the slope of the coexistence curve, which separates liquid phase of the sample from its vapor phase. L is the latent heat that refers to the amount of energy released from the chemical sample. T is the temperature and ΔV is the volume change in the phase transition. Thus, increasing the temperature of the buried sample can significantly improve the detecting time and sensitivity.

To remotely heat up the buried chemical sample, in this paper, microwave heating is employed because it cannot only remotely and quickly heat up the buried samples (because many interested chemicals such as cyclohexanone are polar chemicals) but also overcome the challenge of high attenuation in the soil for other approaches. For example, cyclohexanone, is a polar cyclic ketone that has a dipole moment $\mu = 3.01D$,[9] this natural polarization could lead to the physical rotation of molecular dipoles in the context of microwave electromagnetic radiation. Along with the process of molecular rotation, molecules tend to collide, push, and pull other molecules through electrical forces, which could increase the average kinetic energy of molecules and result in the increase in the temperature of the sample. This effect will become remarkable once the frequency of the electromagnetic radiation comes into the microwave region, because the reorientation of the polar molecules cannot keep pace with the electric field oscillation. As a consequence, the energy from electric field of the radiation could be absorbed into the sample. The re-orientation of the dipoles and displacement of the charge leads to the well known Maxwell displacement

current, which plays a key role for heating the chemical. The permittivity of a medium, ε^*, in a complex form can be written as

$$\varepsilon^* = \varepsilon_0(\varepsilon'_r - j\varepsilon''_r) = \varepsilon' - j\varepsilon'', \tag{3}$$

where ε_0 is the permittivity of the free space while ε'_r and ε''_r are the real and imaginary parts of the relative permittivity. By using this definition, the Maxwell–Ampere equation can take the following form:[10]

$$\nabla \times \vec{H} = \sigma_s \vec{E} + j\omega(\varepsilon' - j\varepsilon'')\vec{E} = (\sigma_s + \omega\varepsilon'')\vec{E} + j\omega\varepsilon'\vec{E}$$
$$= \sigma_e \vec{E} + j\omega\varepsilon'\vec{E}, \tag{4}$$

where the effective conductivity, σ_e, is defined as:[10]

$$\sigma_e = \sigma_s + \omega\varepsilon'' = \sigma_s + \sigma_a, \tag{5}$$

where σ_s is the static field conductivity that is dominant in metal and σ_a is the alternating field conductivity caused by the rotation of the molecular dipoles as they attempt to align with the external field. For many buried chemicals such as cyclohexanone, the value of the static field conductivity σ_s is small. But, under the microwave field, the alternating field conductivity σ_a can be large, which consumes the energy from the applied microwave field and results in an increase in the temperature of the sample. Moreover, we could use the energy conservation equation to describe the energy distribution in a specific volume V:

$$\frac{1}{2}\int\int\int_V (\vec{H}^* \bullet \vec{M}_i + \vec{E} \bullet \vec{J}_i^*)dv$$
$$= \oint\int_S \left(\frac{1}{2}\vec{E} \times \vec{H}^*\right) \bullet ds + \frac{1}{2}\int\int\int_V \sigma_s|\vec{E}|^2 dv$$
$$+ j2\omega\int\int\int_V \left(\frac{1}{4}\mu|\vec{H}|^2 + \frac{1}{4}\varepsilon^*|\vec{E}|^2\right)dv. \tag{6}$$

Equation (6) can be rewritten in the form of

$$P_s = P_e + P_d + j2\omega(\vec{W}_m + \vec{W}_e), \tag{7}$$

where P_s is the supplied power in the region, P_e is the existing power inside the volume, P_d is the dissipated power caused by static field conductivity, which can be neglected when accounting for the chemical heating in the case of this paper. The last two terms in Eq. (7) represent the reactive power associated with the magnetic and the electric fields. Note that, the permittivity of our detected material has a complex value, whose imaginary part will lead to the energy loss. Here we define the alternating electric loss tangent as:

$$\tan\delta_a = \frac{\sigma_a}{\omega\varepsilon'} = \frac{\varepsilon''}{\varepsilon'} = \frac{\varepsilon''_r}{\varepsilon'_r}. \tag{8}$$

If we assume that the applied electric field is homogenous, the generated power density contributing to the heating takes the form of

$$P = \omega\varepsilon_0\varepsilon'_r \tan\delta_a E^2 = \omega\varepsilon_0\varepsilon''_r E^2. \tag{9}$$

From this equation, one can see that the imaginary part of the complex relative permittivity plays a key role during the en-

ergy transformation from the applied electromagnetic field to the heat.

In addition to accelerating the evaporation process via microwave heating described above, another issue is how to quickly transport the microwave generated vapor to the surface of the ground. To realize this goal, we propose to use gradient static electric field generated by a Van De Graaff generator. Furthermore, such a gradient electric field can also serve as a vapor concentrator. Mathematically, this process may be described in the following way. We assume that the interested chemicals are polar chemicals (which are true in most cases). The distance between the two charges is $\vec{d} = \vec{X}_2 - \vec{X}_1$. If the two charges are equal in magnitude but having opposite signs, under the inhomogeneous gradient electric field, the force applied on this dipole takes the form of

$$\vec{F} = q(\vec{E}_1 - \vec{E}_2) = q\{\vec{E}_1 - [\vec{E}_1 + [(\vec{X}_2 - \vec{X}_1) \bullet \nabla]\vec{E}]\}$$
$$= q[(\vec{X}_2 - \vec{X}_1) \bullet \nabla]\vec{E}, \tag{10}$$

where q is the charge, E_1 and E_2 are the electric field at the two charge points, and $\vec{E}$ denotes the general electric field distribution. After introducing the polarization of the dipole $\vec{P} = q(\vec{X}_2 - \vec{X}_1)$, Eq. (10) can be written as

$$\vec{F} = (\vec{P} \bullet \nabla)\vec{E}. \tag{11a}$$

Furthermore, under the linear medium approximation, $\vec{P} = \alpha\vec{E}$, where α is a coefficient. Substituting $\vec{P} = \alpha\vec{E}$ into Eq. (11a), it can be rewritten as

$$\vec{F} = \alpha(\vec{E} \bullet \nabla)\vec{E}. \tag{11b}$$

Equation (11b) can be further simplified by using the following vector analysis identity

$$(\vec{A} \bullet \nabla)\vec{A} \equiv \nabla\left(\frac{1}{2}\vec{A} \cdot \vec{A}\right) - \vec{A} \times (\nabla \times \vec{A}). \tag{12}$$

In this case, the force can be written as

$$\vec{F} = \alpha\left[\frac{1}{2}\nabla(\vec{E} \cdot \vec{E}) - \vec{E} \times (\nabla \times \vec{E})\right]. \tag{13}$$

By using Eq. (13), the force distribution can be calculated and analyzed. The simulation results will be provided in Sec. III.

III. SIMULATION

In the simulation, first, the electric field distribution, $\vec{E}$, from a Van De Graaff generator is calculated. We assume that the globe of the generator is located above the buried chemicals at the position $X = 0.55$, $Y = 0.4$. Figure 1 shows the simulation results. One can clearly see that the electric field intensity, indicated by the line density, radiates from the center of the charged globe of the generator. The closer to the charged globe, the larger the field intensity is. Therefore, a gradient electric field is created surrounding the buried sample. We further assume that the ground surface is located at $Y = 0.2$ and the sample is buried at $Y = 0$. Since the buried chemical is within the inhomogeneous static electric field, the emanated vapor is subjected to the gradient force, as
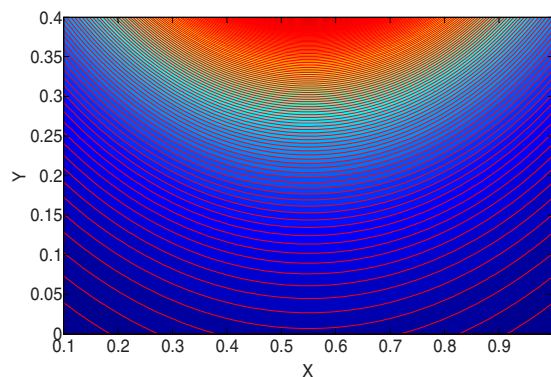
FIG. 1. (Color online) Electric field intensity distribution generated by the charged globe.

given by Eq. (13). To simplify the simulation, we assume that the coefficient α appeared in the Coulomb's electric field equation is normalized to 1 and the units in the simulation are also ignored. Based on Eq. (13), Figs. 2(a)–2(c) represent the forces generated by the gradient electric field acting on the dipole in the vertical y direction and the horizontal x direction, as well as the horizontal force at different vertical y values, respectively. Figure 2(a) reveals that the vapor dipole is subjected to a positive upward force, which pushes the emanated vapor out of the soil and thus accelerates the vapor transport process. This acceleration will be a great help for the real time detection system. Furthermore, it can be noticed that the closer to the charged globe, the larger the upward force will be, and thus, higher acceleration happens near the surface. From Fig. 2(b), one can observe that the force generated by the gradient electric field attempts to attract the released vapors along the gradient to the area of strongest electric field intensity, which is at $X=0.55$. Once the attracted vapors reach the region where the field is the strongest in the x direction, no force is applied on them in the x direction and thus the detected vapor concentration is increased along this line. Thus, this gradient electric field can also serve as a vapor concentrator. Figure 2(c) is another view of the X component of the generated force at different Y values.

Based on our simulation results presented above, it is evident that the gradient electric field can be employed not only to accelerate the vapor transportation process but also to concentrate the vapor, which will be very helpful for increasing both the detection speed and the sensitivity.

IV. EXPERIMENT

To verify the theory developed above and the simulation results, we have also conducted the following experiments. Figure 3 illustrates the schematic configuration of the multifrequency excitation system for detecting the buried and/or concealed chemicals. In the experiment, a microwave source centered at 2.4 GHz with the output power of 1000 W was used to excite the cyclohexanone sample buried in sand soil approximately 3 cm underneath the surface. For the safety reason, both the sample and sand soil were placed inside a microwave waveguide chamber. A hole, from which the emanated vapors could be released, was made on the top of
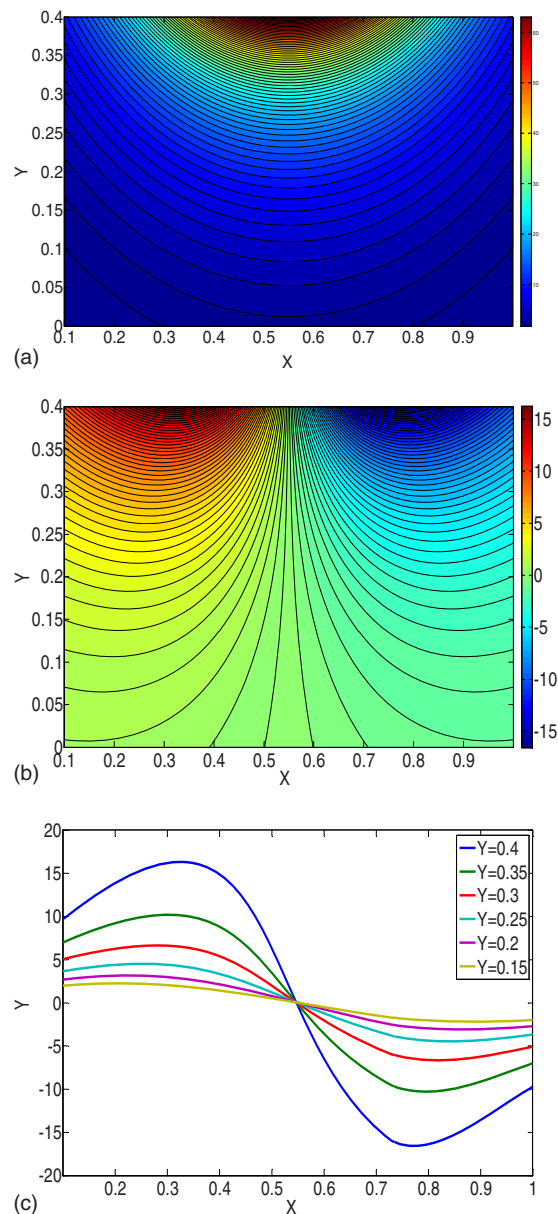

FIG. 2. (Color online) [(a)–(c)] Components of the force generated by the gradient dc electric field in the vertical y direction, in the horizontal x direction, and the x direction field at different y values, respectively.
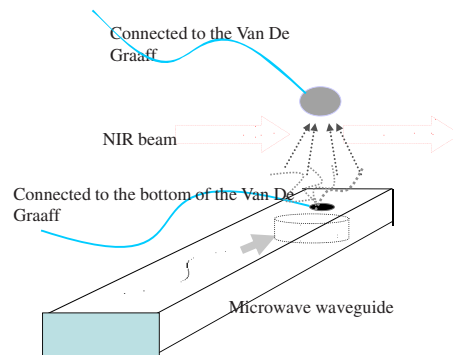

FIG. 3. (Color online) Schematic configuration of the multifrequency based detection system.
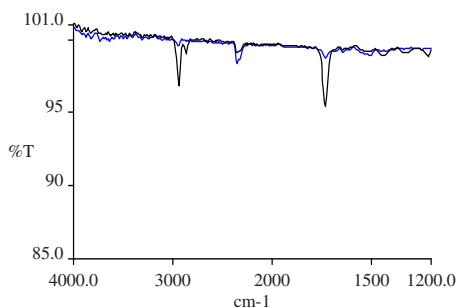
FIG. 4. (Color online) NIR transmission spectra of released chemical vapors without and with gradient dc field excitation.

the waveguide chamber and covered by an aluminum wire net. A metal globe, positively charged by a Van De Graaff generator, was put 5 cm above the hole in order to generate a dc gradient electric field to accelerate and concentrate the emanated vapors. Furthermore, the NIR source in the frequency region from 4000 to 1200 cm^{-1} generated by a Fourier transform IR spectrometer was used to illuminate the emanated vapors. The IR absorption spectra of vapors were measured through the IR absorption characteristics of the released chemical vapors from the hole.

In the detection experiment, the widely used chemical compound cyclohexanone was used, which had two major absorption peaks near 2900 and 1716 cm^{-1}, respectively. For the purpose of comparison, first, we measured the IR absorption spectrum without using microwave and gradient dc fields, as depicted in the blue line of Fig. 4. One can see that there are only very weak peaks near 2900 and 1716 cm^{-1}. The extra peak near 2350 cm^{-1} appeared in Fig. 4 comes from the background CO_2 molecules. Then, by adding the gradient dc electric field, there was a substantial increase (about ninefold) in the magnitude of the absorption peaks, as depicted in the black line of Fig. 4. This experimental result clearly demonstrated that gradient dc electric filed could be used to accelerate the transportation process and to increase the vapor concentration.

In the microwave excitation experiment, first, the power of microwave source was turned on. The blue and black lines of Fig. 5 depict the experimentally measured IR absorption peaks without and with microwave excitations (1 min duration). This experimental results confirmed that microwave excitation could also significantly increase the IR absorption
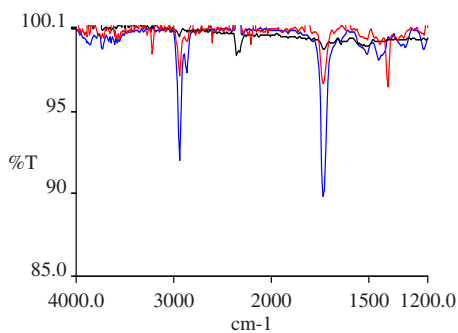

FIG. 5. (Color online) NIR transmission spectra of released chemical vapors with microwave excitation plus dc field excitation for 1 min.
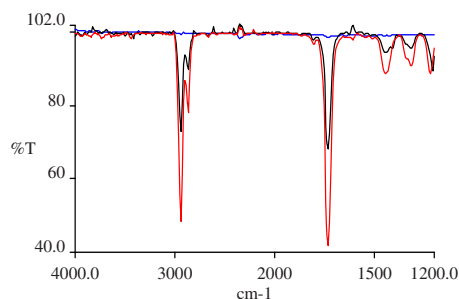

FIG. 6. (Color online) NIR transmission spectra of released chemical vapors with microwave excitation plus dc field excitation for 2 min.

peaks (around sixfold), which verified that microwave excitation could help to accelerate the evaporation process.

Furthermore, we also conducted multifrequency excitation experiment by turning on both the microwave source and the gradient dc electric field. The red line of Fig. 5 depicts the measured IR absorption peaks with both the gradient dc electric field and the microwave excitation (1 min duration). It turned out that more than 20-fold increase in the magnitude of the absorption peak could be obtained in this case. This experimental result demonstrates the advantage of using multifrequency excitation because it can (1) enhance the evaporation process, (2) accelerate the transportation process, and (3) increase the concentration levels simultaneously.

Finally, we investigated the influence of the time duration of microwave excitation. In this experiment, different microwave excitation time was used. It was found that with a longer excitation time, the enhancement in the IR absorption peaks became more significant. For example, Fig. 6 illustrates the measured result after 2 min excitation. Compare Figs. 5 and 6, it is clear that the absorption peaks are increased substantially when the excitation time was increase from 1 to 2 min. Note that, in the real implementations, there can be a tradeoff between the detection speed and the amount of enhancement by employing this multifrequency excitation technique. Different excitation time may be needed for different applications and field circumstances.

V. CONCLUSION

We have developed a new detection system for detecting the buried and concealed chemicals by stimulating and enhancing spectroscopic and imaging signatures with multifrequency excitations, which was composed of low frequency gradient dc electric field, microwave frequency field, and NIR frequencies. The simulation and experimental results confirmed that the gradient dc electric field could be used to accelerate the vapor transportation process and to concentrate the vapors. The microwave excitation could be employed to enhance the evaporation process and to increase vapor concentrations. More than 20-fold increase in the magnitude of IR absorption peaks could be achieved by using the low frequency gradient dc field and microwave frequency field excitation simultaneously. The detection technique presented by this paper can play an important role in many applications such as underground pollution monitoring as well as buried and concealed chemical detections.

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